JOURNAL OF CATALYSIS **146**, 116–125 (1994)

Dispersion Measurement by the Single Introduction Method Coupled with the Back-Sorption Procedure: A Chemisorption and TPD Study of the Different Chemisorbed Hydrogen Species

II. Pd on Alumina

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Received April 27, 1992; revised April 20, 1993

The Single Introduction (S.I.) method for the measurement by hydrogen chemisorption of metal dispersion in supported metal catalysts has been tested on two commercial 5% Pd/Al_2O_3 catalysts. The S.I. results are compared with those obtained by the classical method of determining the adsorption isotherm (i.e., the multiple introduction method) and by O_2/H_2 titration. As in Part I of this work, both chemisorption and thermal desorption have been used to find the best experimental conditions for the "Back-Sorption" procedure. It is shown that α- and β-palladium hydrides can be decomposed by outgassing the samples for less then 5 min at 305 K and 10^{-6} Torr and that 30 min pumping at the same temperature and pressure is sufficient to eliminate from the catalyst surface the weakly adsorbed hydrogen as well. It has also been verified that chemisorption of hydrogen on these catalysts at room temperature is complete at pressures lower than those required for the $\alpha \rightarrow \beta$ phase transition, so that it is possible to perform dispersion measurements by means of a simple S.I. of hydrogen coupled with Back-Sorption below 15 Torr at 305 K. Temperature-programmed desorption of hydrogen on one of the samples outlines the need to discriminate among the different adsorbed species for a more detailed characterization of supported metal catalysts. © 1994 Academic Press, Inc.

INTRODUCTION

Due to the wide use of supported palladium catalysts in chemical industry and the scientific interest of the Pd–H system, many studies have evaluated the metal dispersion D_M ($D_M = n_S^M/n_T^M$, atoms of metal on the surface/total atoms of metal) and the metal surface area MSA (MSA = m^2/g_M, where g_M is the metal weight) of these solids. The most widely used adsorption methods for palladium-based systems are

(a) chemisorption of O_2 and CO (1; 2–5);
(b) chemisorption of H_2, avoiding β-hydride formation (5, 6);
(c) back-sorption (B.S.) of H_2 (adsorption/outgassing/readsorption) (5);
(d) $H_2(D_2)/O_2$ titration and reverse titration (4, 5, 7, 8, 10);
(e) pulse chemisorption of H_2 (kinkpoint method) (9).

In our opinion, method (c) is the most valuable tool to measure the dispersion of palladium catalysts because (i) strongly bound hydrogen (H_S) adsorption stoichiometry is the only one generally accepted to be well-defined on palladium (11, 12), (ii) hydrogen is the species effectively exchanged between the reactants and the catalyst surface in many palladium-catalysed industrial reactions, and (iii) the B.S. technique can provide more information on the state of supported metal than just a measure of its dispersion (13). By contrast, (i) using method (a), CO adsorbs linearly or bridged in different proportions dependent mainly on crystallite size (11, 12) and also it can cause a reduction of the adsorption capacity after successive adsorptions (14), which are often needed to check for repeatability; (ii) the oxygen adsorption stoichiometry used in methods (a) and (d) often depends on the preparation of the catalyst (11); (iii) method (e) does not guarantee the existence of the kinkpoint due to the low accuracy of pulse methods nor does it permit evaluation of the fraction of weakly adsorbed hydrogen (H_w), being a flow technique; (iv) method (b) gives the total hydrogen (H_{TOT}) uptake at the selected equilibrium pressure with no possibility of separating the contributions of weak and strong

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0021-9517/94 $6.00

chemisorption, α-hydride formation, and possibly physisorption.

The aim of this work was to study the optimum conditions to perform hydrogen back-sorption on alumina-supported palladium catalysts, a procedure which, in our opinion, has not been thoroughly examined, and also to evaluate the use of the S.I. method, presented in Part I of this work (13), as a faster and more reliable alternative to multiple introduction (M.I.) isotherms.

Benson *et al.* (5) point out that the back-sorption method becomes unreliable for poor dispersions because the monolayer calculation in the pressure range where β-hydride is stable involves the subtraction of two large quantities with little relative difference, arising from the first and the back-sorption uptakes. In this work we show how to overcome this disadvantage, the chemisorption process being complete before the onset of the $\alpha \rightarrow \beta$ phase transition. Some typical experimental conditions that have been used to avoid β-hydride formation are the following: method (b), 343 K, 1 Torr H_2 (6); method (d), 273 K, 0.4–4 Torr H_2 (4) or 373 K, 350 Torr H_2 and 373 K, 1080 Torr D_2 (5); method (e), 233 K, 2.25 Torr H_2 (9). Our finding is that at 305 K and below 15 Torr only α-hydride and weakly chemisorbed hydrogen can exist in addition to the strongly chemisorbed phase. The calculation of catalyst dispersion is meaningful when only the fraction of hydrogen which adsorbs with a well-defined stoichiometry is considered. This fraction is identified with the strongly bound hydrogen left on the catalysts after the outgassing step in the B.S. procedure. For this species we obtained, from TPD profiles, a desorption energy falling in the range 22–32 kcal/mol, in accordance with the values measured for the desorption of hydrogen from the most densely packed single crystal surfaces whose adsorption stoichiometries have been carefully determined (15a). Strictly speaking, following the removal by pumping of the so-called reversible species (H_{REV}), the species remaining on the catalyst surface are defined in a purely empirical way as irreversibly bound hydrogen (H_{IRR}). Nevertheless, under the assumptions already discussed in Part I (13), n_S^H can be taken as equal to n_{IRR}^H, where the letter n indicates gas uptake.

EXPERIMENTAL

Materials and instrumentation. Catalysts studied were 5% Pd/γ-Al_2O_3 powder (Type 207 R/D, Lot N.8362), designated sample A, and 5% Pd/Al_2O_3 $\frac{1}{8}$-in. pellets (Type 221 N/D, Lot No. 2683), designated sample B, both kindly loaned by Degussa. Each catalyst batch contained 1.0–1.5 g of material. Hydrogen was of the same type as reported in Part I (13) and oxygen was cylinder gas, purity 99.995%. Instruments for hydrogen chemisorption and thermal desorption have already been described (13). H_2/O_2 titrations were performed in a conventional all-glass volumetric apparatus. Water produced during the titration was removed with 1.0 g of dry calcium sulphate ($CaSO_4 \cdot 2H_2O$, Merck), calcined at 623 K overnight before use. XPS measurements were done with the same apparatus as cited in Part I (13).

Preparation and treatment of samples. All measurements (S.I. and M.I. chemisorptions, TPD, H_2/O_2 titrations) were performed after a cleaning procedure consisting of a reduction treatment in flowing hydrogen (60 N $cm^3 \cdot s^{-1} \cdot g_M^{-1}$) at 373 K for 3 h followed by the evacuation of the samples at 573 K and 10^{-6} Torr for 16 h. The reduction temperature was the lowest able to cause the disappearance of all the characteristic peaks of oxidized palladium in the photoelectron spectra of both catalysts so that, at the measured sensitivity level of the ESCA system, a reduction degree better than 99.5% could be estimated. The evacuation temperature was set higher than those corresponding to all TPD peak positions and the duration of this operation was chosen to be equal to the time needed to lower the mass spectrometer signal of hydrogen below the background value (hydrogen partial pressure lower than 10^{-8} Torr). The above-mentioned reduction/outgassing pretreatment proved to be a suitable cleaning procedure for alumina-supported catalysts, this oxide being inactive with respect to strong metal–support interactions (15b, 16) which could give rise to spillover phenomena.

Hydrogen chemisorption and back-sorption. All chemisorption measurements were carried out at 305 K. Gas/solid systems were left to equilibrate for 30 min after each gas introduction (17) in all S.I., M.I., and H_2/O_2 titrations. In the outgassing step following the first adsorption in the Back-sorption (B.S.) procedure, the pumping time, t_{BS}, was kept to the value of 30 min. In fact, as determined with TPD experiments (see below), only the strongly bound hydrogen, irreversibly adsorbed on the catalyst, is left on the surface after 30 min pumping.

Thermal desorption. All TPD experiments were made on sample A, with a constant heating rate of 10 K/min to increase the mass spectrometer signal for quantitative analysis (18a). This caused a lower peak resolution compared with that attainable with a heating rate of 5 K/min (13, 18a). Using very finely dispersed powder (particle mean diameter lower than 400 mesh) and a high pumping speed, v_p, we could rule out kinetic effects due to internal diffusion and readsorption (19, 20).

Hydrogen titration. After the adsorption of hydrogen at 305 K, at pressures well above those needed for the $\alpha \rightarrow \beta$ phase transition (final equilibrium pressure >600 Torr), and subsequent evacuation for 30 min at the same temperature and 10^{-6} Torr, a classical oxygen adsorption

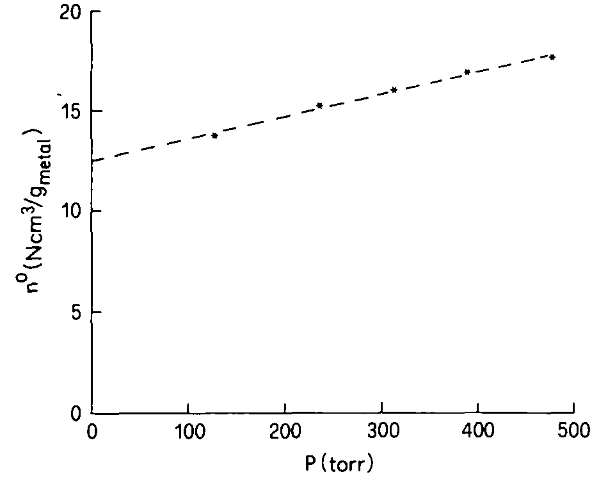

FIG. 1. Oxygen titration at 300 K of hydrogen adsorbed on sample A. Hydrogen adsorption was performed at 300 K under an equilibrium pressure of 600 Torr. The sample was then evacuated at 10^{-6} Torr for 30 min. at the same temperature prior to titration.

isotherm was recorded until an equilibrium pressure of 480 Torr was reached. The resulting curve for sample A is shown in Fig. 1.

RESULTS AND DISCUSSION

Hydrogen Chemisorption and Back-Sorption

In order to evaluate the accordance between M.I. and S.I. results for the same catalyst batch (the calculation of the monolayer volume, V_m, taken equal to n^H_{IRR}, has already been described in Part I (13)), we checked whether the thermal treatment (T.T.) in the sequence reported in Fig. 2 could lower the metal surface area by sintering, as observed by Konvalinka and Scholten (9). The comparison shown in Table 1 of the hydrogen uptakes obtained with the complete above-mentioned sequence do demonstrate the occurrence of sintering during the usual thermal treatment (heating from the reduction temperature to 573 K at a rate of 10 K/min at 10^{-6} Torr and further outgassing at the same temperature and pressure for 16 h). For this reason, the comparison between M.I. and S.I. methods was made on different batches of catalyst with particular care being given to the weighing step preceding the experiments (13).

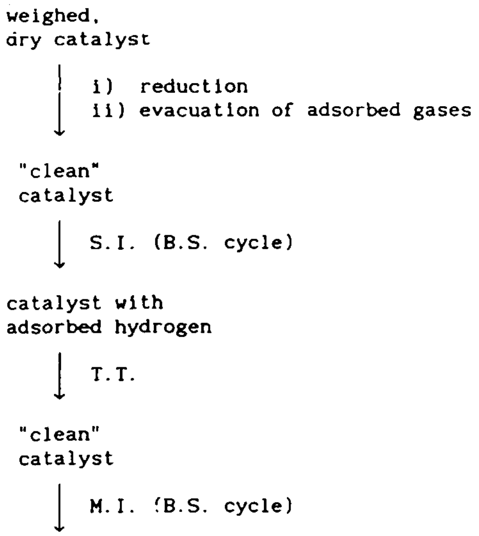

FIG. 2. Experimental sequence for the comparison of M.I. and S.I. results. T.T. stands for the thermal treatment between the two adsorption procedures (see text).

Aiming at determining a pressure range suitable for dispersion calculation which avoids β-hydride formation, and inspecting the M.I. curve shape in order to apply the S.I. technique (13), we recorded M.I. hydrogen isotherms at 283, 305, 323, and 343 K at maximum equilibrium pressures ranging from 6.5 to 325 Torr, as shown in Fig. 3. These isotherms, similar to others already published (21–24), are consistent with the expected variation of the $\alpha \rightarrow \beta$ phase transition pressure and the α- and β-hydride uptakes with the adsorption temperature (25, 26). We found that a temperature close to room temperature was high enough to monitor the strong chemisorption process from the beginning to its completion in the pressure range 1–15 Torr, where only the α-hydride exists and where modern 100 Torr full-scale capacitative manometers give their best performances. In fact, assuming that $n^H_S \cong n^H_{IRR}$ (13), curve C in Fig. 4, which represents the irrevers-

TABLE 1

Data for Single Introduction (S.I.) and Multiple Introduction (M.I.) Methods with Back-Sorption (B.S.) Showing Effect of the Thermal Treatment (T.T., See Text) Between Successive Chemisorption Measurements at 305 K on Sample A

	Uptake (N cm^3/g$_M$)				
	S.I. (B.S. cycle)	T.T. ⟶	S.I. (B.S. cycle)	T.T. ⟶	M.I.[a] (B.S. cycle)
n^H_T	13.49		13.42		—
n^H_{REV}	5.83[b]		6.42[b]		—
n^H_{IRR}	7.66[c]		7.00[c]		6.50[d]

Note. S.I. Uptakes at Equilibrium Pressures Lower Than 15 Torr. n^H_T is the total hydrogen uptake, obtained from the first of each pair of measurements; n^H_{REV} is the reversible uptake from the second one; and n^H_{IRR} is the irreversible fraction, set equal to the monolayer volume, V_m.

[a] From a logical point of view, it is not correct to include M.I. uptakes alongside the S.I. ones in the comparison of results, the equivalence of the two methods being the subject of this work; but, as demonstrated in the text, the accordance between the M.I. and S.I. methods is actually so good as to justify, in practice, this position.

[b] Pressure-dependent values in the range 0–60 Torr.

[c] Pressure-independent values above 3 Torr.

[d] Same irreversible uptake in the ranges 6–11 and 50–60 Torr.

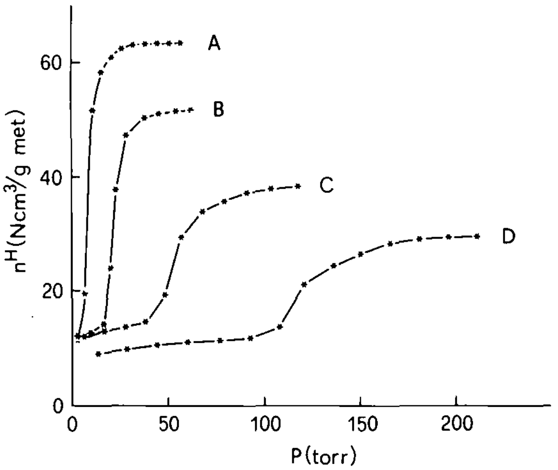

FIG. 3. M.I. hydrogen isotherms for sample A at increasing adsorption temperatures: A, 283 K; B, 305 K; C, 323 K; D, 353 K.

ible hydrogen uptake on sample A at 305 K, as obtained by subtraction of curve B from curve A, related to the Back-Sorption (n^H_{REV}) and the first (n^H_T) uptakes, respectively, demonstrates that H_S chemisorption is complete at pressures lower than that required for the $\alpha \rightarrow \beta$ phase transition, p_t, n^H_{IRR} being the same before and after p_t. An estimate of the amount of weakly adsorbed hydrogen at $p < p_t$ can thus be obtained as $n^H_W = n^H_{REV} - n^H_{H,\alpha}$, where the last term is the amount of hydrogen forming the α-hydride, which can be calculated using Sievert's law (27, 28). Furthermore, as evidenced in Fig. 4, the slopes of both curves A and B are sufficiently low, in the α-phase region, to permit a comparison of S.I. and M.I. results (13). It should be noted that the slope of the isotherm at 323 K, curve C in Fig. 3, is even lower than that of curve B, but at this temperature the attainable separation of weak and strong chemisorption is worse (29). For these reasons, all chemisorption experiments were performed at 305 K. S.I. chemisorptions at 305 K on sample A are reported in Fig. 5. Phase transition pressures, p_t (Torr), and adsorption temperatures, T (K), were correlated in the range 283–343 K through an Antoine-like expression, giving the following result (linear correlation coefficient $r > 0.999$):

$$\log_e(p_t) \cong 18.58 - 4667 \cdot T^{-1}. \qquad [1]$$

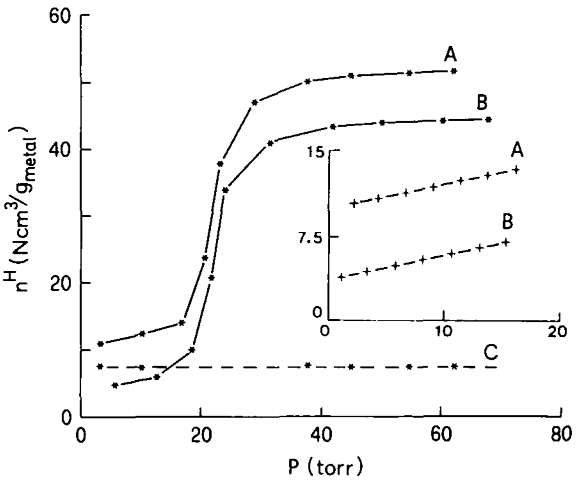

FIG. 4. M.I. hydrogen isotherm with back-sorption for sample A. Adsorption temperature was 305 K. Curve A: total uptake; curve B: reversible uptake after evacuation for 30 min at 305 K and 10^{-6} torr; curve C: irreversible uptake. In the inset a low-pressure measurement is shown.

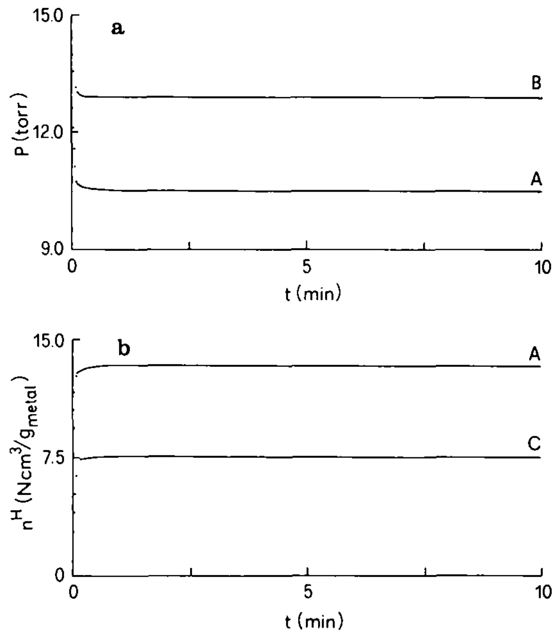

FIG. 5. S.I. hydrogen isotherms with Back-Sorption for sample A. Adsorption temperature was 305 K. (a) Pressure vs time curve; (b) adsorbed amount vs time curve. Curve A: first adsorption; curve B: second adsorption after evacuation for 30 min at 305 K and 10^{-6} Torr; curve C: irreversible uptake.

Equation [1], which has already been used in the past for bulk palladium (30), could be useful to evaluate the maximum working pressure, at the given adsorption temperature, to avoid β-hydride formation on Pd/Al_2O_3 catalysts during the chemisorption measurement.

Thermal Desorption

In Fig. 6a we report a series of TPD profiles obtained after adsorption of increasing amounts of hydrogen and successive cooling down to 193 K without any pumping prior to the beginning of the analysis (however, the gas over the sample was eliminated with 1 min pumping at

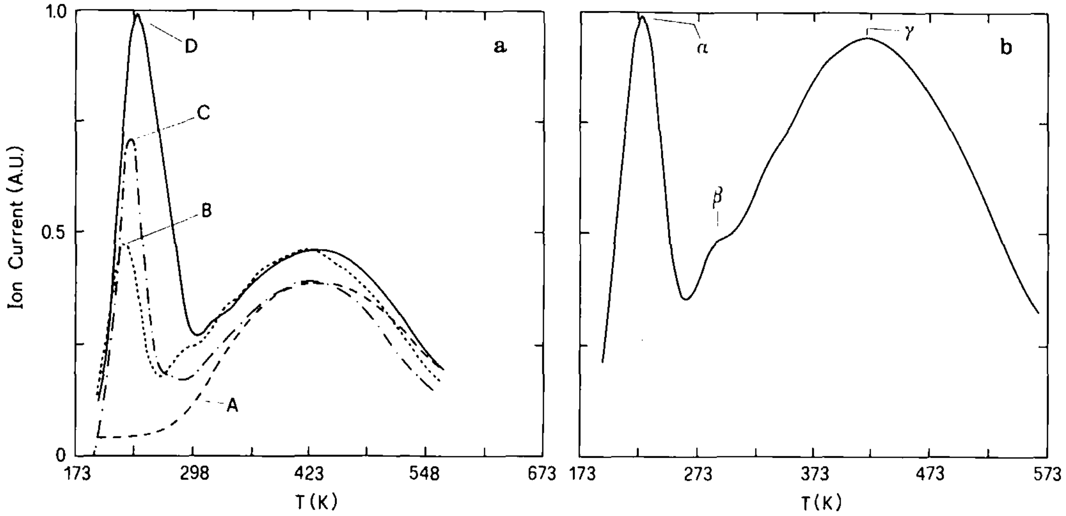

FIG. 6. Thermal desorption of H_2 from sample A after adsorption at 300 K. (a) Effect of equilibrium pressure on the low-temperature peak: A, 0.04 Torr; B, 9.76 Torr; C, 59.1 Torr; D, 574 Torr. All profiles were obtained after 1 min evacuation at 300 K to remove the gas phase and subsequent cooling to 193 K prior to desorption. (b) Detail of curve B in Fig. 6a showing the three main peak groups on Pd/Al_2O_3: α, palladium hydrides; β, weakly bound hydrogen; γ, strongly bound hydrogen.

193 K, i.e., with the Outgassing step in Fig. 6 of Ref. (13)). These curves may be regarded as the TPD analogues of the adsorption isotherms shown in Fig. 3. Figure 6b illustrates in detail curve B of Fig. 6a. Three peaks (α, β and γ) are evident in Fig. 6b with maxima (T_M) centered at the temperatures of 228, 300, and 423 K, respectively.

Peak α has its maximum located at temperatures very close to the one corresponding to the α_2 peak (T_M = 225 K) obtained by Ertl and co-workers after hydrogen adsorption at 130 K on Pd(110) (31, 32) and to peak α reported by Aldag and Schmidt (Fig. 3, Ref. (33)), both attributed to the desorption of subsurface hydrogen (H_{SS}). Hydrogen uptakes calculated by integration of peak α are in fairly good accordance with the estimates drawn from the adsorption isotherms, so that we agree with these authors in assigning this peak to desorption of hydrogen dissolved in palladium crystallites (H_B). It can be noted that we assign peak α here indifferently to H_B and H_{SS}, although these species should be considered as quite distinct (15c). In fact, as H_B diffuses to the surface, passing through the subsurface region, it cannot be distinguished from H_{SS} by TPD experiments (15d). The activation energy for the desorption of H_B, calculated using the crude formula given by Knor (34), E_d(kJ/mol) $\cong 0.23 \cdot T_M$(K), provides a value of about 12 kcal/mol, in accordance with the value of 11–13 kcal/mole reported in Ref. (33), but obtained in a different way. This finding further strengthens our interpretation of peak α.

By analogy with the desorption profile for the H_2–Pt/Al_2O_3 system, reported in Part I (peak C in Fig. 5, Ref. (13)), peak β is attributed to weakly chemisorbed hydrogen. This peak is similar to the one reported by Konvalinka and Scholten (peak A in Fig. 4, Ref. (9); T_M = 293 K) for hydrogen desorption from a Pd/C catalyst, attributed to the desorption of subsurface hydrogen. Figure 7a shows how it was possible to resolve this feature by lowering the catalyst temperature to about 190 K even after the system had attained equilibrium conditions at a pressure considerably lower than that used to obtain peak B in Fig. 6b (0.045 and 9.76 Torr, respectively). To obtain some insight into the characteristics of weakly bound hydrogen, we measured a series of thermal desorptions of hydrogen from a sample of palladium black. The specimen, produced by Engelhard, purity 99.95% (the remaining 0.05% consisting of carbon contaminants with no trace of alkaline metals, as verified through elemental analysis), was reduced in flowing hydrogen at 373 K before the first measurement and outgassed at 623 K and 10^{-8} Torr for 12 h before each adsorption/desorption cycle. In Fig. 8 we report a series of thermal desorption profiles at increasing initial coverage, following adsorption at 193 K. The series in Fig. 8a and Fig. 8b are the same; Fig. 8b with each curve normalized on a different ion-current scale, is shown only to enhance peak resolution. With reference to Fig. 8b, the maxima of peaks α_D, β_C, and γ_A are located at the same temperatures as the corresponding peaks in Fig. 6b so that their assignment is the same as for supported palladium. In particular, the position of peak β_C demonstrates that weak hydrogen is effectively adsorbed on the *metal* surface, as in the case of platinum (35). Furthermore, the shift of the weak hydrogen peak toward higher temperatures, in the order $\beta_A > \beta_B > \beta_C$, clearly reveals that the H_W desorption kinetics are second order with respect to surface coverage (18a,

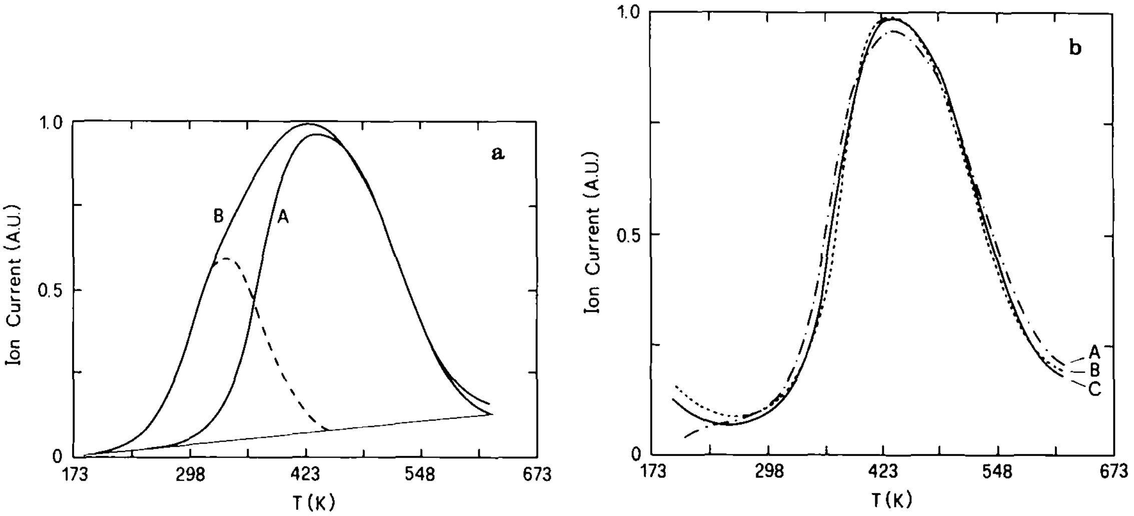

FIG. 7. Thermal desorption of H_2 from sample A after adsorption at 300 K. Initial pressure was 1.44 Torr and final equilibrium pressure was 0.045 Torr. (a) Curve A was obtained after evacuation of the sample for 30 min at 300 K and 10^{-6} Torr and successive cooling to 193 K; curve B was obtained with no pumping prior to desorption so that weakly bound species could be left on the catalyst surface. Profile deconvolution is intended to be only qualitative. (b) Effect of increasing pumping times, t_{BS}, on the strongly bound hydrogen peak: A, 5 min; B, 30 min; C, 75 min.

36). Finally, as evidenced in Fig. 8a, weakly bound species begin to populate the metal surface only after the completion of the strongly held monolayer, as observed for the other Group VIII transition metals studied in Part I. A calculation of the desorption activation energy for H_W with the simplified formula of Knor gives a value of about 16 kcal/mol. A further estimate with Eq. [2],

$$(1/n) \cdot \theta_M^{(n-1)} = (k_d \cdot T_M \cdot a_M^{-1}) \cdot E_0(x_M) \qquad [2]$$

$$r_d = -(d\theta/dt) = k_d \cdot \theta^n \cdot \exp[-E_d/RT], \qquad [3]$$

where n is the desorption order, θ_M is the surface coverage at peak maximum, k_d is the frequency factor (s^{-1}) appearing in expression (3) for the desorption rate, a_M is the heating rate (K/s), and $E_0(x_M) = \exp(-x_M)/x_M$ with $x_M = E_d/RT_M$, was obtained by Smutek for the case of a homogeneous surface with no readsorption (18b). It gives

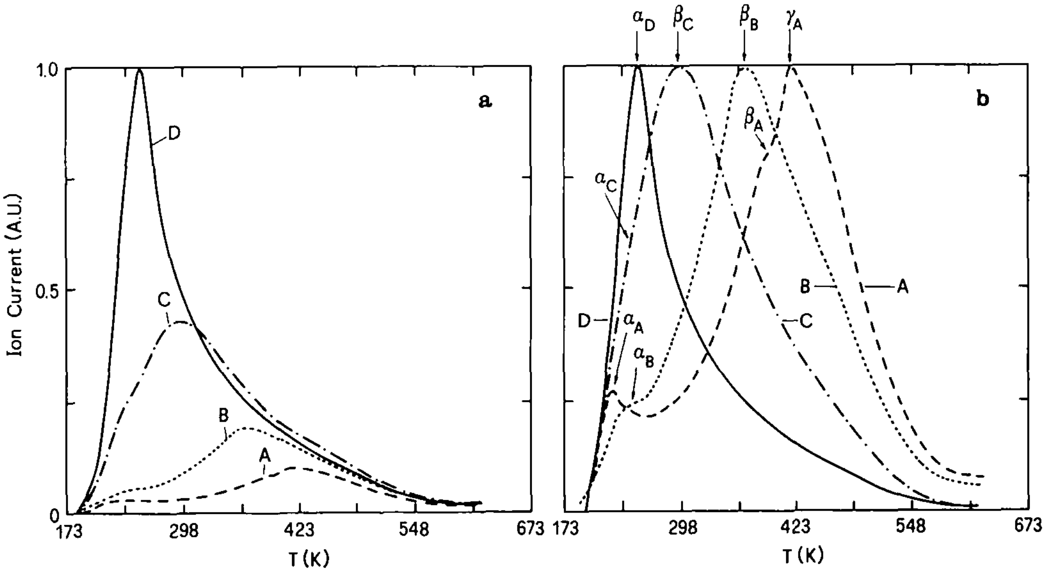

FIG. 8. (a) Thermal desorption of H_2 from Pd black after adsorption at 193 K of 0.025 (A), 0.05 (B), 0.1 (C), and 0.15 (D) N cm^3 H_2/g_{Pd}. (b) Some profiles as shown in Fig. 8a but with each curve normalized to unity to resolve the fine structure. Peaks α, β, and γ are assigned to $H_{H,\alpha}(H_{SS})$, H_W, and H_S, respectively.

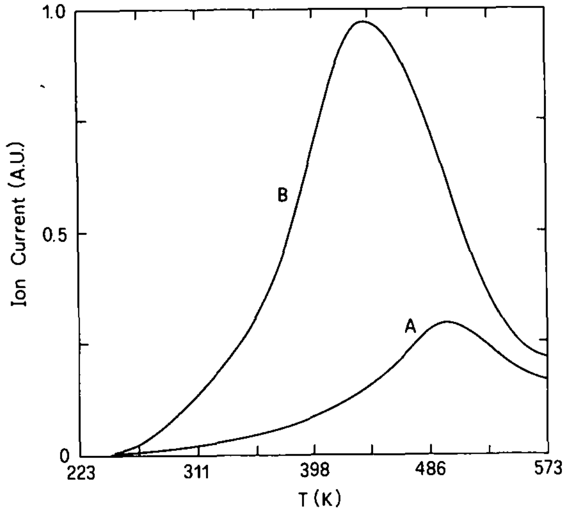

FIG. 9. Thermal desorption of H_2 from sample A after adsorption at 243 K and successive outgassing at the same temperature and 10^{-6} torr for 30 min. Equilibrium pressure was: A, 0.011 Torr; B, 0.045 Torr.

a value of about 20.5 kcal/mol when $n = 2$, $\theta_M = 0.5$ (Eq. (31) of Ref. (18b) enabled us to calculate θ_M and E_d in a self-consistent way), $k_d = 10^{13}$ s^{-1} (36) and $a_M = 10$ K/min. We can finally estimate a mean desorption energy for H_W falling in the range 16–21 kcal/mol.

Peak γ is very similar to that reported by Aldag and Schmidt for a polycrystalline palladium filament (peak β in Fig. 3, Ref. (33); $T_M \cong 400$ K) and also to that appearing in the paper of Konvalinka and Scholten (peak B in Fig. 4, Ref. (9); $T_M = 407$ K). This peak is generally attributed to bimolecular desorption of strongly bound hydrogen. The peak shape and the shift of its maximum to lower temperatures with increasing coverage, as shown in Fig. 9, demonstrate the order of desorption (18a, 36). A detailed calculation for peak γ, which unlike peak β could be isolated through a suitable sample evacuation or by chemisorption at low pressure, has been performed using the method of Tokoro *et al.* (37) for heterogeneous surfaces with no readsorption. Energy profiles like that shown in Fig. 10 could be obtained. The activation energy for the desorption of strongly bound hydrogen varies in the range 22–32 kcal/mol, in good agreement with the data reported by Aldag and Schmidt ($E_d(\gamma) = 22$–35) Kcal/mol (33)) and in accordance with what is expected for a highly heterogeneous polycrystalline surface.

As already mentioned in Part I (13), the main purpose of the B.S. procedure is the elimination from the catalyst surface of all the reversible species, which are not useful for the calculation of the *monolayer uptake*, V_m. In particular, some of these (see Eqs. (5) to (8) in Ref. (13)) are weak *surface* species which must be eliminated both because the adsorption stoichiometry of weakly adsorbed hydrogen is greatly dependent on the crystallite structure (38–40) (although, in principle, the stoichiometric coefficient for weak hydrogen adsorption, SF_W, which gives the number of surface metal atoms which bind a single weak hydrogen atom could be obtained by suitable spectroscopic analyses (38, 41)) and, which is more important, because most of the H_W is probably coordinated to surface metal atoms belonging to "ensembles" that already constitute the adsorption sites for H_S, these last being "counted" once already by n_S^H. In the case of palladium, the correctness of the equality $V_m \cong n_S^H \cong n_{IRR}^H$, which permits one to calculate D_M through the equation $n_S^M = SF_m \cdot V_m \cong SF_{IRR} \cdot n_{IRR}^H$ (13), where SF_m is the stoichiometric coefficient related to the saturation of the monolayer, depends not only on the conditions $n_{REV,m}^H \ll n_S^H$ and $n_R^H \ll n_S^H$ but also on the effect produced by H_{SS}. In fact, H_{SS} is thought to exit from the subsurface region by coupling with hydrogen atoms chemisorbed at the surface (breakthrough mechanism (9, 42)). If this process involves some of the H_S atoms, as asserted in Ref. (9), the equality $n_{IRR}^H \cong n_S^H$ can no longer hold, these strongly chemisorbed hydrogen atoms being desorbed with H_{SS} and not present on the surface as irreversibly bound species. In our opinion, this is not the case for the catalyst studied in the present work. In fact, under the assumption that $H_{H,\alpha}$ diffuses toward the surface by passing through the subsurface layer, i.e., hopping into the H_{SS} adsorption sites, peak α in Fig. 6b effectively represents the desorption of H_{SS} and the corresponding desorption energy

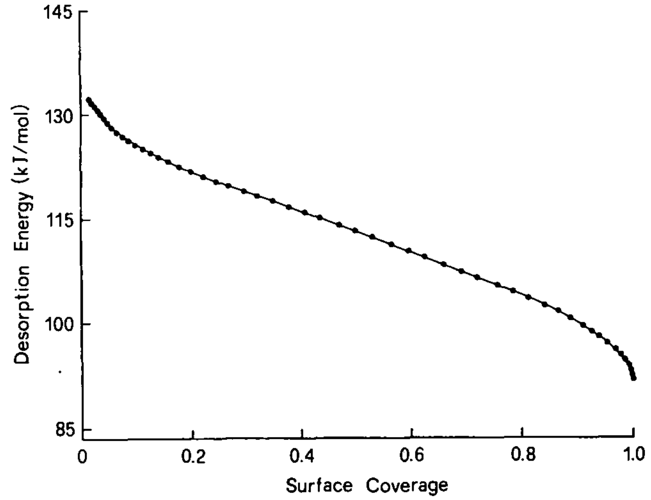

FIG. 10. Variation of desorption activation energy, E_d, with surface coverage calculated for strongly chemisorbed hydrogen on sample A with the model of Tokoro et al. (37). Circles mark the values of E_d calculated by solving the set of linear equations (2) in Ref. (40) while the continuous line is the analytical desorption energy distribution function as obtained by least-squares fitting of the same E_d values with the coverage power-series expansion (3) in Ref. (40).

($T_M(\alpha)$ = 225 K) proves to be considerably lower than that for peak A in Ref. (9) (T_M = 293 K). This would mean that on our sample A the coupling of H_{SS} involves atoms bound at the surface less strongly than H_S, i.e., H_W or even H_M (15d). Incidentally, this would also explain the rather low ratios n_W^H/n_S^H observed for palladium in Fig. 6b as compared with the values reported in Part I (13) for Pt, Ru, and Rh. We are at present working to demonstrate this hypothesis. Good results have been obtained by means of computer simulations (43); we have found that TPD peaks centered around 220 K can indeed arise when a nonzero H_{SS} concentration in the subsurface layer, ζ, is introduced among the boundary conditions at time t = 0 (44). This position was not discussed by Leary *et al.*, who set $\zeta = 0$ at $t = 0$ in their demonstration that H_{SS} gives rise to a peak at temperatures higher than those related to H_S (44).

In the case of alumina-supported palladium, the thermal desorption experiments allow for a rather sharp identification of the correct conditions to be used in the B.S. procedure. In fact, the intermediate outgassing at 300 K (which is almost coincident with $T_M(\beta)$ in Fig. 6b) is able to isolate the H_S peak in 5 min pumping with no further effect on the peak area due to longer times, as evidenced in Fig. 7a and Fig. 7b, showing the effect of pumping on the multiplicity of peaks in the high-temperature region of the profile. All TPD profiles reported in Fig. 7 were obtained after adsorption at 305 K under an equilibrium pressure of 0.045 Torr. It is interesting to note that, the surface coverage being constant during pumping from 5 to 75 min (see Fig. 7b), we expect a similar independence of the surface state from the particular pumping speed of the given chemisorption apparatus. This overcomes the main drawback of the B.S. procedure, i.e., the practical impossibility of using vacuum systems with the same fundamental characteristics in different laboratories. The possibility of isolating with such clarity only the H_s peak through B.S. should be mainly ascribed both to the rather large difference in mean desorption energies between H_w and H_s ($\Delta\bar{E}_d \approx$ 10 kcal/mol) had to a quite sharp distribution of the H_W desorption energies. In this work we could not calibrate our chemisorption experiments against a standard palladium catalyst, as we did for platinum with EUROPT-1 (13), so that the correctness of the *joined* position SF_{IRR} = 1 *plus* $V_m \cong n_{IRR}^H \cong n_S^H$ could not be tested. Nevertheless, the unambiguous isolation of a well-defined TPD peak corresponding to H_s, which is the only condition needed for a consistent measurement of D_M, should be taken by itself as a successful application of the B.S. procedure.

Comparison of M.I., S.I., and Titration Methods

MSA, D_m, and V_m values obtained with the above-mentioned techniques for adsorption at 305 K on samples A and B are reported in Table 2. As for Pt, Rh, and Ru (13), the S.I. results are in good agreement with those drawn from M.I. measurements so that, for palladium as well, the former method could be a valid alternative to the latter. A possible explanation for the slightly higher results obtained with oxygen titration as compared with the S.I. and M.I. results could be a partial subsurface oxidation (bulk oxidation of palladium at the adsorption temperature used can be ruled out (8)), which shifts the O_2/H_2 titration stoichiometry from the theoretical value of 1.5 (used in Table 2) to a value in the interval from 1.65 to 1.85. A partial reduction (and successive reoxidation during titration) of the support during the cleaning procedure would be rather improbable (10). A further possible reason for this overestimation of the monolayer uptake could be the titration of residual hydrogen. Incidentally, a true advantage of the O_2/H_2 titration technique is its capability to provide an estimate for n_R^H whenever the value for the titration stoichiometry can be safely taken as equal to 1.5.

TABLE 2

Comparison of Results Obtained With M.I., S.I., and O_2 Titration using B.S. Procedure

	Method		
	M.I.	S.I.	O_2 titration[a]
	Sample A		
V_m(N cm^3 H_2/g_M)[b]	7.5	7.7	8.3
100 · D_M[c]	7.1	7.3	7.9
MSA (m^2/g_M)[d]	31.7	32.6	35.1
	Sample B		
V_m(N cm^3 H_2/g_M)	20.0	21.2	25.7
100 · D_M	19.0	20.1	24.4
MSA (m^2/g_M)	84.6	89.7	108.7

[a] Based on the equation 2 Pd–H + $\frac{3}{2}$ $O_2 \rightarrow$ 2 Pd–O + H_2O (6).

[b] $V_m \equiv n_{IRR}^H$ (irreversibly bound hydrogen (13)).

[c] D_M = surface metal atoms/total metal atoms = $K_1 \cdot$ MSA $\cdot$ MW $\cdot\, \sigma^{-1}$, where MW is the molecular weight of metal, σ is the mean area occupied by a surface metal atom (Å^2), and the constant $K_1 \cong 1.66 \times 10^{-4}$ (mol · Å^2 · m^{-2}).

[d] MSA = $K_2 \cdot V_m \cdot$ SF $\cdot\, \sigma$, where SF is the stoichiometric factor (surface metal atoms/irreversibly adsorbed gas molecules) and the constant $K_2 \cong 0.2687$ (m^2 · Å^{-2} · N cm^{-3}). The values SF = 2 (*14*) and σ = 7.87 Å^2 (*11*) were used.

All isotherms recorded on the two samples show that the amount of strongly bound hydrogen can be calculated both in the α-phase formation region and in the β-phase completion region with the same results (see curve C in Fig. 4). This means that the outgassing step in the B.S. procedure effectively removes all the reversibly bound hydrogen (including the bulk hydrogen) and that it is not necessary to attain high pressures during adsorption ($p > p_t$) nor very low pressures (e.g., Aben's $p \sim$ 1 Torr) to measure dispersion. A maximum equilibrium pressure of, say, 15 Torr (where a commonly used 100 Torr full-scale capacitive manometer gives best readings) at a temperature near 300 K proves to be more suitable.

CONCLUSIONS

In the thermal desorption profile of a commercial supported palladium catalyst (5% Pd) three distinct peaks are clearly visible in the range 173–673 K. These peaks have been assigned to α-(β-) hydride decomposition, weakly bound hydrogen, and strongly bound hydrogen. After the samples are outgassed at 305 K and 10^{-6} Torr for 30 min, only the latter is still present on the surface, so that these experimental conditions can be used to calculate metal dispersion by means of the Back-Sorption procedure.

The Single Introduction results are in fairly good accordance with those drawn from the classical adsorption isotherms, as already observed with other supported Group VIII metals (13). It is demonstrated that the fraction of strongly bound hydrogen can be calculated from a simple S.I. measurement at 305 K below 15 Torr, the irreversible adsorption in this pressure range being completed. This avoids the need to perform dispersion measurements in the unusual 1 Torr region suggested by Aben (6) and overcomes the problem of the large relative errors involved in the calculation of surface-to-bulk uptakes in the high pressure region, where also the β-hydride phase exists. In any case, for a highly dispersed catalyst these errors are not significant, so that a dispersion measurement in the β-phase completion region is also feasible. The rapidity (analysis times lower than for M.I. by an order of magnitude) and reproducibility of the S.I. method coupled with the B.S. procedure make this technique a valid alternative to the existing ones for dispersion measurements of palladium catalysts (at least those supported on alumina).

Further study of the many surface hydrogen species and, in particular, of weakly chemisorbed hydrogen on real catalysts could enable one to achieve more information on the structure of supported metals.

ACKNOWLEDGMENTS

The financial support of C.N.R. "Progetto Finalizzato Chimica Fine" is gratefully acknowledged.

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