

Stoichiometry of the Titration by Dihydrogen of Oxygen Adsorbed on Platinum

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The adsorption of dihydrogen and oxygen, as well as the titration by dihydrogen of adsorbed oxygen, was studied volumetrically on platinum powder free of contaminants as determined by Auger electron spectroscopy. The numbers of adsorbed H and O atoms per surface Pt atom are 1.1 and 0.71, respectively. A standard procedure for measurement of the percentage metal exposed for supported platinum is proposed. © 1990 Academic Press, Inc.

INTRODUCTION

The dispersion of platinum on different supports has been studied repeatedly during the past 20 years. However, there is no universally accepted technique to measure the exposed platinum area. The selective chemisorption of gases, principally dihydrogen and carbon monoxide, provides a simple experimental procedure to estimate the area of the exposed metal. Unfortunately, when the surface area of the metal is small, correction for the support adsorption may be large enough to impair the results. This limitation prompted Benson and Boudart (1) to develop a titration technique. By preadsorbing oxygen on the supported metal at room temperature and subsequent titration with dihydrogen to form water, three hydrogen atoms are consumed per exposed platinum atom, thus tripling the sensitivity for hydrogen adsorption. On the basis of adsorption results on platinum powder, it was proposed that one surface platinum atom Pt_s adsorbs one oxygen atom O_a or one hydrogen atom, H_a . This stoichiometry was immediately challenged by Mears and Hansford (2), who accepted the ratio $O_a/Pt_s = 1$ on supported platinum but argued in favor of H_a/Pt_s ratios of about 2, because although the product water of the

titration would migrate to a hydrophilic support, it would be retained on the surface of platinum powder, thus preventing the adsorption of a second hydrogen atom. To check this interpretation, Vannice *et al.* (3) reinvestigated the adsorption of hydrogen and oxygen on platinum powder, observing ratios O_a/Pt_s and H_a/Pt_s close to 1 at room temperature. They concluded that water is displaced from the platinum surface by dihydrogen at room temperature. Their work supports the stoichiometry proposed by Benson and Boudart.

Next, the effect of platinum crystal size on adsorption stoichiometries was emphasized by Wilson and Hall (4), who observed that growth of platinum particles supported on alumina did not change the H_a/Pt_s value of unity, while the O_a/Pt_s ratio increased with increasing metal particle size. The authors concluded that the titration of an oxygen covered surface could be in error by about 16%, depending on crystal size. In later work on titration technique, no consensus was reached (5-7). An extensive review of the chemisorption techniques has been presented by Karnaukhov (8).

However, some of the previous experiments carried out on platinum powder may have been impaired by contamination of the metal surface by potassium (9). We decided to undertake the present work because of the availability of a platinum powder pre-

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pared and studied in our recent work (9). This powder exhibits a clean surface as evidenced not only by Auger electron spectroscopy but also by a turnover rate for hydrogenation of cyclohexene characteristic of clean platinum. Therefore this powder provides the opportunity of measuring the stoichiometry of chemisorption.

EXPERIMENTAL

Materials and Apparatus

All experiments were carried out on platinum powders derived from a 50-g lot (#11379) of Engelhard platinum powder. These powders were washed in concentrated nitric acid and reduced in dihydrogen as described elsewhere (9). The Auger electron transitions observed in the powders thus prepared were only those corresponding to platinum. A conventional fixed volume glass apparatus, described elsewhere (9), was used. Matheson Research Grade dioxygen was used as such, while Liquid Carbonic Hi-Purity Grade dihydrogen was purified by passage through a Milton Roy palladium thimble. A cold finger at 195 K was used to trap the water formed during the titration and remove it from the gas phase.

Methods

The acid washed powders were evacuated at 0.001 Pa for 30 min at room temperature and for an additional 30 min at 392 K. Platinum powders are much more sensitive to sintering when exposed to dihydrogen than supported platinum. It was noted that the surface area of the powder was inversely proportional to the rate of exposure. To minimize the loss of surface area, the initial exposure of the powders to dihydrogen was done at low controlled rates. The final reduction was carried out in static dihydrogen at 20 to 50 kPa for $\frac{1}{2}$ h at 398 K, followed by evacuation at 0.001 Pa and 398 K for 16 h. At higher temperature the powder sinters rapidly as verified by BET sur-

face area measurements using argon as adsorptive (9).

Stoichiometric ratios were measured at temperatures between 195 and 346 K. The experimental routine was as follows: oxygen adsorption at temperature T ; evacuation for 15 min at T to remove gas phase dioxygen; hydrogen titration of the adsorbed oxygen at T ; evacuation at 398 K; hydrogen adsorption at T ; evacuation at room temperature for 15 min to remove gas phase dihydrogen; BET surface area measurement; final reduction and evacuation to restore the surface conditions prevailing before oxygen adsorption.

During the adsorption experiments, the pressure reached a steady-state value (saturation) within 2 h after the first dose. Nevertheless, to assure that saturation was established, the pressure was recorded only 24 h after the start of adsorption. Following subsequent doses, saturation pressure was reached within 1 min and was recorded after 30 min.

To prove that no surface oxygen was desorbed in the evacuation directly following adsorption of dioxygen, the latter was adsorbed at 195 K on a sample of the powder. This sample was then evacuated for 20 h at room temperature. A backdesorption isotherm performed after this long evacuation showed only 10% of the initial uptake. Thus, oxygen adsorbed on platinum does not appear to be removed in significant amounts by the brief evacuation for 15 min at room temperature.

RESULTS

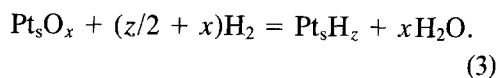
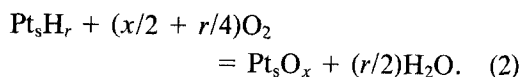
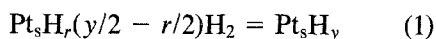
All isotherms were horizontal between 1 and 50 kPa, indicating negligible physisorption. Uptake values measured at the various temperatures are collected in Table 1.

Vannice *et al.* (3) have called the quantities that describe the chemisorption of hydrogen and oxygen the stoichiometric ratios. These ratios are shown below in the hydrogen adsorption, oxygen adsorption, and hydrogen titration reactions, respectively:

TABLE 1

Chemisorption of Hydrogen and Oxygen on Platinum Powder for Adsorption (Subscript a) and Titration of O_a by H₂ (Subscript t)

Adsorption temperature/(K)	Argon BET area (m ² g ⁻¹)	Specific uptake (μmol g ⁻¹)		
		O _a	H _t	H _a
195	13.6	194	574	178
273	12.8	222	622	168
298	16.4	268	760	210
298	12.3	228	608	168
298	11.3	212	578	158
346	14.9	272	722	168



The stoichiometric ratio of hydrogen chemisorption y is the number of adsorbed hydrogen atoms per surface platinum atom Pt_s. The stoichiometric ratio of oxygen chemisorption x is the number of adsorbed oxygen atoms per Pt_s. The stoichiometric ratio of hydrogen chemisorption in the titration, z , may be different from y . Because of the temperature limit during reduction and evacuation (398 K) imposed by the instability of the platinum surface area, the removal of hydrogen from the surface is not complete and this hydrogen must be taken into account. The ratio r represents the number of adsorbed hydrogen atoms per surface platinum atom after the evacuation. When r and the total surface area are known, the ratios y , x , and z can be calculated from the uptake values in the hydrogen adsorption, oxygen adsorption, and hydrogen titration referred to as H_a, O_a, and H_t, respectively (Table 1). It should be noted that the sum of 2O_a plus H_a is equal to H_t within 2% for all temperatures between

195 and 346 K. As will be shown later, this equality means that y is equal to z . In all calculations, the platinum surface atom number density was assumed to be 1.19×10^{15} cm⁻², the arithmetic average for the three low index planes of platinum (I).

In order to measure r , dideuterium was substituted for dihydrogen in the reduction of the sample. Following the final evacuation, the dihydrogen uptake was measured. From a mass spectrometric analysis of the gas in contact with the powder and a BET surface area measurement, the value of r was calculated to be 0.40 ± 0.02 . Since the final evacuation procedure was always used prior to the oxygen and hydrogen adsorption measurements, r was always assumed to be 0.40. The stoichiometric ratios were calculated from the results of Table 1. Between 273 and 298 K, the ratios x and y are 0.71 ± 0.06 and 1.10 ± 0.08 , respectively.

DISCUSSION

Methods

Various chemisorption methods have been reported in the literature for the determination of the stoichiometric ratios and for routine determination of % metal exposed, E . For the determination of the stoichiometric ratios, the chemisorption technique should minimize the introduction of impurities. In addition, the chemisorption conditions, i.e., temperature, pressure, and equilibrium time, should be well defined. But a method used for the routine determination of metal dispersion should be fast, reproducible, and consistent with the method used to measure the stoichiometric ratios.

Two common flow methods have been used to study chemisorption: the pulse adsorption and the continuous flow method. These may be acceptable for routine measurements *if properly calibrated*, but they are not suitable for the measurement of stoichiometric ratios. In the former, the pressure of the adsorptive cannot be defined and the saturation may not be estab-

TABLE 2

The Stoichiometric Ratio, y , of the Chemisorption of Hydrogen on Unsupported Platinum

Type of platinum	T (K)	P (kPa)	y	Reference
Black	195–346	1–50	1.10	This work
Black	523	32	0.86	17
Black	523	13	0.78	16
Black	523	13	0.86	18
Black	273	0.01	0.75	19
Black	298	6.6	0.86	3
Black	298	0.13	0.88	21
Film	78	0.001	0.88	20
Film	90	0.0001	0.94	14
Powder	273	0.266	1.20	22
Raney	300	50	1.4	23
Pt(111)	230	UHV	0.9	24
Pt(111)	150	UHV	0.8	25

lished. In the latter, the state of chemisorption can be defined, but it lacks the accuracy of the volumetric method (2). Also, flow methods involve passage of large volumes of carrier gas over the sample, increasing the risk of contamination. Significant differences in values of % metal exposed obtained with pulse and static adsorption techniques have been reported (7). There are three methods which meet the requirements for the determination of the stoichiometric ratios: volumetric adsorption, gravimetric measurements, and isotopic exchange in a volumetric apparatus. In the following, we shall discuss only results obtained by these three methods.

Hydrogen Chemisorption

(a) *Unsupported platinum.* Early studies of hydrogen chemisorption on platinum (10–14) were performed prior to the development of the BET method; therefore the authors could not report absolute values for y . Nevertheless, these studies are interesting since they show that H_a (and by inference y) vary with the temperature and pressure of the chemisorption. Later studies (Table 2) measured values of y . Although most of these authors worked at lower pres-

ures and higher temperatures than those used in the present work, their reported y values are reasonably close to ours. It should be noted that most platinum powders might have been contaminated with alkali metals (9), as we found 0.24 and 0.33 wt% potassium (9) in the powders used by Benson and Boudart (1) and by Vannice *et al.* (3), respectively. This contamination could lead to values of y lower than 1 (9). Experiments carried out on platinum films and single crystal planes tend to result in values of y closer to 1. Norton *et al.* (24) used deuterium instead of dihydrogen in their work. They report that the value of y for deuterium would be somewhat larger than that expected for hydrogen because of the larger heat of chemisorption of the heavier species.

(b) *Supported Pt.* Several comparisons have been made of the platinum area average particle size calculated from hydrogen chemisorption and the number average particle size measured by transmission electron microscopy (4, 19, 26, 27, 28) or the volume average crystallite size measured by X-ray line broadening (17, 19, 26, 29, 30) and by X-ray small-angle scattering (27, 31, 32). When the particle size measured by hydrogen chemisorption is compared with the crystallite size measured by the X-ray techniques, two implicit assumptions are made, namely, that all particles are single crystallites and that the different averaging methods yield the same result. The results presented in Fig. 1 show good agreement between particle size measured by H_2 chemisorption assuming $y = 1$ and those measured by the independent techniques. However, the stoichiometry may vary for very small particles ($d\hat{p} < 1.5$ nm) (33).

Oxygen Chemisorption

(a) *Unsupported platinum.* The stoichiometric ratio of oxygen chemisorption, y , has been studied both on unsupported and supported platinum. As in the case of hydrogen adsorption, early studies (10, 12,

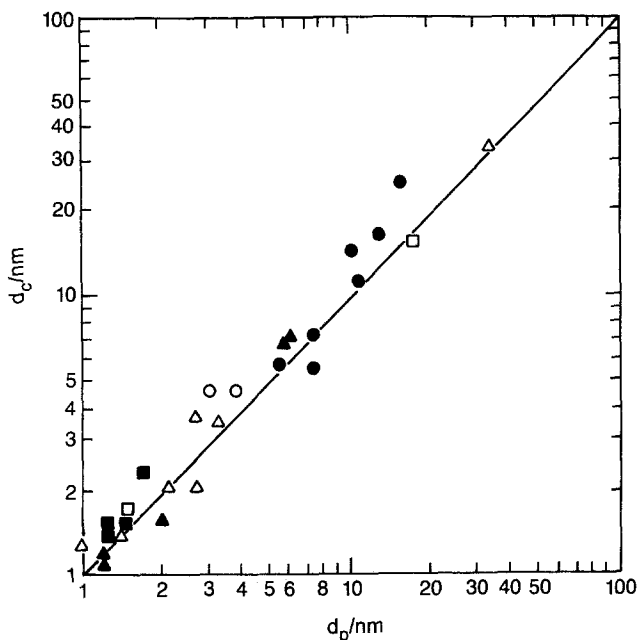


FIG. 1. Supported platinum particle size as measured by hydrogen chemisorption (d_c) assuming a stoichiometric coefficient $\gamma = 1$ and measured by transmission electron microscopy, X-ray line broadening, and X-ray small-angle scattering (d_p). Symbols denote the sources of the data: open circles (19), full circles (29), open triangles (26), full triangles (32), open squares (28), and full squares (4).

34) showed that the ratio x varied with temperature and pressure.

Several studies of oxygen chemisorption carried out in equipment satisfying the requirements specified above are listed in Table 3. It can be seen that most workers obtained values for the ratio x close to those found by us, although their experimental conditions were often far removed from ours. In particular, the data reported by Brennan *et al.* (35), Barteau *et al.* (38), and McClellan *et al.* (39) are within 15% of our value for x . It should be noted that Brennan *et al.* worked with evaporated platinum films that can be considered to be reasonably clean, while the other authors used clean, well-defined single crystal planes. The low stoichiometric ratio found by Sandler and Durigon (36) could have been due to preadsorbed oxygen. High values for x have been reported by Benson and Boudart (1) and by Vannice *et al.* (3). However, Benson and Boudart failed to correct

their data for r , and both studies were carried out on platinum powders contaminated with potassium. It has been shown recently (41) that potassium promotes the chemisorption of oxygen on platinum, leading to O/Pt_s ratios close to 1. Numerous authors have studied the chemisorption of oxygen on various types of platinum surfaces using ultrahigh vacuum techniques and several experimental probes, as reviewed by Gland (40). This author reported values for x between 0.25 and 0.5; however, Barteau *et al.* pointed out that the main experimental obstacle to achievement of high oxygen coverage on platinum was the efficient clean off reaction by background dihydrogen and carbon monoxide. By minimizing the clean off and increasing the temperature, these authors observed larger values of x . Griffiths *et al.* (42) observed that high oxygen pressures and high temperatures are needed in order to reconstruct the Pt(100) surface to a "complex" phase where high

TABLE 3

The Stoichiometric Ratio, x , for the Chemisorption of Oxygen on Unsupported Platinum

Type of platinum	T (K)	P (kPa)	x	Reference
Black	195–346	1–50	0.71	This work
Black	298	1.2	0.37	36
Black	298	66	1.1	1
Black	298	2.6	0.84	3
Film	298	HV	0.65	35
Raney	300	50	0.8	23
Raney	373	0.007	0.58	37
Pt(111)	585	UHV	0.68	38
Pt(321)	285	UHV	0.6	39
Pt(111)	100	UHV	0.25	40
Pt(111)	300	UHV	0.95	41
covered with K				
Pt(100)	640	UHV	0.63	42

oxygen coverages ($x = 0.63$) can be obtained.

(b) *Supported platinum.* The chemisorption of oxygen on supported platinum has generally been measured relative to the chemisorption of hydrogen. There are many studies of the relative uptake of dihydrogen and dioxygen in the literature, as shown in Table 4. The ratio of dioxygen to dihydrogen uptakes, O_a/H_a , should then be equal to x on supported catalysts which have been evacuated at temperatures high enough for r to be 0. The ratio of O_a to H_a derived from our measurements of x and y is 0.65. Again, we see that our results are well within the range of the literature data. The ratio O_a/H_a seems to be definitely less than 1, and most often between 0.4 and 0.8. The results with this ratio greater than 0.8 were, for the most part, obtained on alumina supports with severe reduction. Oxygen may be removed from the alumina support, if it is partially reduced by the severe reduction, resulting in abnormally high values for x .

The Ratio for Titration of O_a by H_2

When oxygen and hydrogen chemisorption and hydrogen titration measurements

are made on a new system (novel support, contaminated samples, alloys, etc.), the pretreatment conditions needed to get a suitable surface are not known with certainty. There exists a relationship between the three uptakes (H_a , O_a , and H_t) that can be used to check the consistency of the uptake values and to demonstrate the suitability of the pretreatment conditions. The uptake values of oxygen chemisorption, hydrogen titration, and hydrogen chemisorption are related to the stoichiometric ratios in Eqs. (1) to (3) as follows,

$$O_a = S(r/2 + x) \quad (3)$$

$$H_t = S(2x + z) \quad (4)$$

$$H_a = S(y - r), \quad (5)$$

where S , the amount of Pt_s (in μmol per g of sample), is determined from BET measurements and the assumed platinum surface atom density. Eliminating r and S from the above equations, we can write

$$R_t = \frac{H_t}{2O_a + H_a} = \frac{x + z/2}{x + y/2}, \quad (6)$$

defining R_t as the titration ratio. Relationships similar to Eq. (6) have been suggested in the literature (46, 47). For all our measurements on the Pt powder R_t was within 2% of unity. The simplest interpretation of a set of adsorptions in which R_t is unity is

TABLE 4

Oxygen and Hydrogen Chemisorption on Supported Platinum

Support	H_a/Pt_s	O_a/H_a	Reference
$\gamma\text{-Al}_2\text{O}_3$	0.68–0.93	0.44–0.53	2
$\gamma\text{-Al}_2\text{O}_3$	0.64–1.13	0.35–1.00	43
$\eta\text{-Al}_2\text{O}_3$	0.51	0.50	2
$\eta\text{-Al}_2\text{O}_3$	0.98–1.20	0.54–0.61	43
Al_2O_3	0.23–0.97	0.46–1.02	4
SiO_2	0.08–0.11	0.71–0.83	43
SiO_2	1.03	0.46	2
SiO_2	0.28–0.88	0.59–1.08	26
SiO_2	0.88–0.97	0.58–0.61	26
CaY-zeolite	1.14	0.51	44
NaY-zeolite	0.98	0.44	32
Alon (Cabot Corp.)	0.61–0.73	0.43–0.49	45
Graphon	0.35	0.77	43

that y and z are equal. Although R_t could be unity for y and z unequal, an unlikely second situation must then compensate precisely for the difference between y and z .

There are several possible experimental situations that can result in values of the titration ratio different than 1. If part of the adsorbed oxygen is removed by the evacuation at room temperature which precedes the hydrogen titration, or if only part of the adsorbed oxygen is reduced in the titration, R_t would be less than 1. This last situation can occur when part of the oxygen reacts with the support. If the adsorbed oxygen reacts with hydrogen to form $Pt_3(OH)$, then R_t would be at most 0.5 when y is equal to 0. Sintering of the metal surfaces during evacuation at 398 K between the hydrogen titration and hydrogen chemisorption would result in R_t values greater than unity.

Volumetric measurements will be inaccurate if the water produced in the titration reaction remains in the vapor phase. This situation was avoided in our experiments by use of a cold trap. Work on supported catalysts may not require the cold trap because the water produced is probably adsorbed by the support. Hydrogen may react with or spill over the support during the hydrogen titration or oxygen chemisorption. However, if the amount of hydrogen that reacts with or spills over on the support is the same in the hydrogen titration and in the hydrogen chemisorption, R_t would still be unity, but the values of y and z would be too large.

The possibility that product water will remain on the platinum surface at room temperature, as suggested by Mears and Hansford (2), can be reasonably ruled out in the light of recent experimental evidence. Sexton (48) observed that water adsorbs on Pt(111) at 100 K and desorbs at 160 K. Fisher and Gland (49) verified that water adsorbs molecularly on Pt(111) at 100 K and desorbs with maximum rate at 165 K and at 180 K for monolayer and multilayer coverage, respectively. These authors noted that preadsorbed oxygen increased

the peak water desorption temperature by 35 K. This finding was examined in detail by Fisher and Sexton (50), who observed that water adsorbed at 100 K desorbs at 180 K without dissociation, but in the presence of adsorbed atomic oxygen, water dissociates above 150 K to form adsorbed hydroxyl species. These species show a broad desorption peak at 215 K, that is, 35 K above the pure water desorption peak.

Next we will discuss two examples in the literature in which R_t is not unity. Wilson and Hall (4) made a thorough study of the effect of the reduction conditions on O_a , H_t , and H_a for platinum dispersed in alumina. As they increased the reduction temperature from 573 K to above 900 K, the platinum particle size increased as shown both by hydrogen chemisorption and electron microscopy. They also studied the ratio of O_a/H_a , which is equal to x/y , since r was zero in their study, observing that O_a/H_a increased from 0.5 to 1.2 as the platinum particle size increased. Wilson and Hall interpreted these results as an increase in x with the increase in particle size. However, another process happened at the same time as the particles grew during the high temperature reduction. After reduction above 900 K, R_t is significantly less than unity. It appears that following a severe reduction, all the oxygen which adsorbs at room temperature is not removed by a subsequent room temperature titration. This phenomenon has been observed by Kobayashi *et al.* (6). Perhaps the severe reduction forms oxygen vacancies in the alumina support. These vacancies may be reoxidized by the oxygen chemisorption, but are not formed again by the room temperature titration. A similar proposal has been made by Den Otter and Dautzenberg (51). In another study, Wilson and Hall (26) investigated the effects of the reduction conditions on the chemisorption of oxygen and hydrogen for platinum supported on silica gel. As in their previous study, O_a/H_a increased from 0.6 to 1.0 as the reduction severity increased, causing particle growth. For all the data in

this study, R_t was within 9% of unity. It appears as if silica gel does not readily form oxygen vacancies when severely reduced, but alumina does.

Kikuchi *et al.* (45) studied a modification of the hydrogen titration where both hydrogen titration and chemisorption were performed at room temperature, but the temperature of the oxygen chemisorption was varied from room temperature to 773 K. When all measurements were made at room temperature, O_a/H_a was near 0.5 and R_t was unity. When the temperature of the oxygen chemisorption was increased, O_a/H_a increased and approached unity, but R_t was increasingly less than unity. Kikuchi *et al.* believe that oxygen adsorbed at temperatures above room temperature cannot be reduced by a subsequent room temperature titration. This conclusion is probably correct, and it shows that the entire sequence of titration measurements on platinum should be made at room temperature, as proposed by Benson and Boudart (1).

Most of the discrepancies in the reported value of the stoichiometric ratios can now be understood. The results presented in this work show a ratio $x/y = 0.65$, similar to that proposed by Mears and Hansford $x/y = 0.5$. Benson and Boudart, as well as Wilson and Hall, report larger values for the ratio x/y , probably due to over-reduction of the catalyst leading to removal of oxygen from the alumina support. Potassium in the platinum powder used by Vannice *et al.* could have decreased the amount of hydrogen chemisorbed, leading to values of x/y close to 1.

In future studies of oxygen and hydrogen chemisorption on platinum, all three quantities, O_a , H_t , and H_a , should be measured. The titration ratio, R_t , calculated from these three values should be used to check the conclusions of the present work.

CONCLUSIONS

Two methods are widely used to determine the percentage of platinum exposed in hydrogen chemisorption and hydrogen ti-

tration. The former presents the advantage of simplicity and a better established stoichiometry. Its main drawback is the need to heat the sample at high temperatures to desorb hydrogen. In the titration, more hydrogen is taken up for each surface platinum atom. Thus the limit of detection of surface platinum atoms is improved. Besides, the measurement is made on an oxidized surface, which can be obtained at low temperatures and may be easier to reproduce than a reduced surface. However, the titration may yield erroneous results if the metal surface is contaminated, e.g., with sulfur (52).

The dispersion can be calculated as

$$E (\% \text{ metal exposed}) = \frac{1.95H_t}{(2x + y)W} \quad (7)$$

where H_t is the hydrogen uptake in the titration (in $\mu\text{mol g}^{-1}$), x and y are the stoichiometric ratios of chemisorbed oxygen and hydrogen, respectively, and W is the weight percentage of platinum in the sample. The values measured for platinum powder, $y = 1.10$ and $x = 0.71$, should be used to interpret the titration results. There seems to be a consensus in the literature regarding the value of y ; but x appears to vary between 0.5 and 0.7. At any rate, this is not a serious problem: even if x varied from 0.5 to as high as 1.0, the percentage metal exposed, calculated by Eq. (8), would be in error by 20% only. Highly dispersed platinum ($E = 100\%$) presents values of y varying between 1 and 2 (53). In these cases the value of E obtained from Eq. (7) will be larger than 100% but should be reported as equal to 100%. In order to measure H_t we recommend the procedure in Table 5 for volumetric adsorption systems. This procedure would work for Pt on supports that retard sintering (Al_2O_3) but would not work for Pt powders and might not work for other supports (carbon).

The reduction and evacuation times (steps 4 and 5) are shorter than the times used by Benson and Boudart (1), in view of the results of Wilson and Hall (4, 26).

TABLE 5
Recommended Procedure to Measure H_t

Step	Procedure	Purpose
1	Evacuate at RT for $\frac{1}{2}$ h	Remove air
2	Evacuate at 398 K for $\frac{1}{2}$ h	Remove water
3	Expose to flowing H_2 at $0.5 \text{ cm}^3/\text{s}^{-1} \text{ g}^{-1}$ at 398 K and heat to 775 K	Reduce the Pt
4	Hold for 1 h at 775 K in flowing H_2	Reduce the Pt
5	Evacuate for 1 h at 775 K	Remove gas phase H_2 and all the adsorbed H
6	Cool to RT while evacuating	Prepare for adsorption
7	Expose the sample to atmospheric pressure O_2 at RT	Oxidize the surface
8	Evacuate for $\frac{1}{4}$ h at RT	Remove gas phase O_2 and leave adsorbed O intact
9	Measure H_t at RT	

Note. RT stands for room temperature.

Impurities, like potassium in the untreated powder, may increase the amount of oxygen chemisorbed in step 7. This interference can be evaluated from a measurement of the amount of oxygen chemisorbed and a measurement of the amount of hydrogen chemisorption, H_a . If the ratio of O_a to H_a is greatly different from 0.65, impurities

TABLE 6

Completion of Recommended Procedure to Measure H_a When the Value of R_t (Titration Ratio) Is Suspected of Being Different from Unity

Step	Procedure	Purpose
7	Measure O_a at RT	
8	Evacuate at RT for $\frac{1}{4}$ h	Remove gas phase O_2 and leave adsorbed O intact
9	Measure H_t at RT	
10	Heat to 775 K in flowing H_2 and hold for 1 h	Reduce the Pt
11	Evacuate for 1 h at 775 K	Remove gas phase H_2 and all the adsorbed H
12	Cool to RT while evacuating	Prepare for adsorption
13	Measure H_a at RT	

Note. RT stands for room temperature.

may be present. If the value of R_t calculated from O_a , H_t , and H_a is different from unity by more than 5%, the support may be partially reduced, or other problems may be present. If interference is suspected, H_a , O_a , and H_t should be measured and the titration ratio used to confirm the consistency of the results. Steps 7 to 9 are replaced by the procedure shown in Table 6.

Finally, we hope that the procedure presented will be checked by a number of independent laboratories on the same sample, in the fashion of the characterization studies carried out recently on the EUROPT-1 catalyst (54).

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