JOURNAL OF CATALYSIS 16, 348-356 (1970)

Determination of Surface Area by Chemisorption: Unsupported Platinum

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Received July 10, 1969

The adsorption of hydrogen and oxygen, as well as the reaction of hydrogen with adsorbed oxygen, was studied gravimetrically and volumetrically on platinum black. The water formed during the reaction leaves the surface and as it does so, it is not replaced by additional hydrogen. The amount of hydrogen adsorbed is the same on a reduced and evacuated surface as it is on a preoxidized surface. The ratio of adsorbed hydrogen and oxygen atoms to surface platinum atoms is close to unity at room temperature and a pressure of 50 torr.

INTRODUCTION

Supported platinum catalysts are of great importance in theory and in practice. For quantitative measurements it is essential to know the surface area of the metal. The latter can be determined by selective chemisorption techniques using hydrogen, oxygen, or carbon monoxide. In each case it is necessary to know the stoichiometry of the surface reaction, i.e., the relation between the number of surface platinum atoms, Pt_s, and the number of adsorbed atoms or molecules.

For instance, the stoichiometric ratios x, y, and z can be defined as follows:

$$Pt_s + \frac{x}{2} O_s \rightarrow Pt_s - O_x, \quad (1)$$

$$Pt_s + \frac{y}{2} H_2 \rightarrow Pt_s - H_y, \quad (2)$$

$$Pt_s - O_x + (x + \frac{z}{2})H_2 \rightarrow Pt_s - H_z + xH_2O. \quad (3)$$

Values of either x or y are required in a determination of the surface area of platinum by chemisorption of oxygen or hydrogen on a prereduced and evacuated platinum surface. These *adsorption* techniques, especially with hydrogen, are in frequent use today. Both the values of x and z are necessary in the *titration* [represented by Eq. (3)], consisting of the measurement of the number of molecules of hydrogen taken up by a platinum surface on which oxygen has been preadsorbed.

Values of x, y, and z may well depend on a variety of experimental variables such as temperature, pressure, crystal size and habit. Besides, the question as to whether y is equal to z has been raised recently by Mears and Hansford (*1*). From adsorption and titration measurements performed on supported platinum catalysts, these authors suggest, in particular, that y may not be the same as z unless the water formed in the titration reaction is removed by a hydrophilic support. They further suggest that this situation might be that prevailing on platinum black, where z values should be less than y values because unremoved water prevents further adsorption of hydrogen.

Because Mears and Hansford did not report any data with platinum black and because these are important in establishing stoichiometric ratios, we decided to undertake the present work. A survey of the literature, restricted to unsupported platinum (Tables 1 to 3), amply justifies the need for such an investigation. In partic-

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ular, values of y from 0.13 to 0.97 have been reported on various samples of unsupported platinum metal prepared and used under a variety of conditions. A value of y equal to two has even been inferred by Mears and Hansford from early data of Benton (*2*) with platinum black.

Unfortunately, Benton did not have BET surface area values for his samples. The main advantage of using unsupported platinum in the study of stoichiometric ratios is precisely that the number of surface platinum atoms can be determined independently by the BET measurement. All ratios of Tables 1 to 3 have been recalculated when necessary from the original data by assuming 1.19×10^{15} cm^{-2} as the average density of platinum sites. This value corresponds to the average area per platinum atom for the three low-index planes of the metal.

There are, however, two severe drawbacks in the use of platinum black. First, it sinters readily so that reproducible data on a given sample are hard to obtain. In the present work we found that, if adsorption and titration were initiated at or below 210°K, platinum black lost very little surface area from run to run.

A second difficulty, related to the ease with which platinum black sinters, is that hydrogen remains on the surface after low

TABLE 1

STOICHIOMETRIC RATIO, y, OF HYDROGEN ADSORPTION ON PLATINUM

Authors	Ref.	y	P(torr)	T(°C)	Sample	BET adsorbate
Benton	(*2*)	—	760	25	Black	—
Sieverts and Bruning	(*4*)	—	750	−120 to 200	Black	—
Maxted and Hassid	(*5*)	—	760	−200 to 100	Black	—
Kwan	(*6*)	0.13	1	280	Black	N_2
Boreskov and Karnaukhov	(*7*)	0.97	240	250	Black	Ar
Boreskov and Vasilevich	(*8*)	0.95	10^{-3}	−183	Film	Kr
Adler and Keavney	(*9*)	0.61	—	200	Foil	—
Spenadel and Boudart	(*10*)	0.92	240	250	Black	Ar
Gruber	(*11*)	0.87	100	250	Black	N_2
Adams *et al.*	(*12*)	0.73	—	0	Black	—
Ponec *et al.*	(*13*)	0.88	$\leq 10^{-2}$[a]	−195	Film	Kr and Xe

[a] Personal communication from V. Ponec.

TABLE 2

STOICHIOMETRIC RATIO, x, OF OXYGEN ADSORPTION ON PLATINUM

Authors	Ref.	x	P(torr)	T(°C)	Sample	BET adsorbate
Benton	(*2*)	—	760	25	Black	—
Brennan *et al.*	(*14*)	0.67	$<10^{-4}$	25	Film	Kr
Benson and Boudart	(*15*)	0.91	500	25	Black	N_2
Sandler and Durigon	(*16*)	0.76	9	25	Powder	Kr
Walter *et al.*	(*17*)	0.65	5×10^{-2}	100	Raney	—

TABLE 3

STOICHIOMETRIC RATIO, $x + (z/2)$, OF HYDROGEN TITRATION ON PLATINUM

Authors	Ref.	$x + \frac{z}{2}$	P(torr)	T(°C)	Sample	BET adsorbate
Chon *et al.*	(*18*)	1.47	—	0	Black	N_2
Boudart *et al.*	(*19*)	1.42	500	25	Foil	Kr

temperature reduction and evacuation. This may account for too high values of x and too low values of y reported in Tables 1 and 2. To correct for this residual hydrogen, we used hydrogen–deuterium experiments similar to those employed by Hall and Lutinski (*3*).

In addition to conventional volumetric measurements, we have made parallel gravimetric measurements by replacing hydrogen with deuterium. The use of deuterium in the gravimetric work was felt to be highly desirable because of increased sensitivity in the weighings. This combination of gravimetric and volumetric measurements is particularly flexible and useful since one type of measurement, while acting as an independent check of the other, gives additional information. For example, the gravimetric method permitted us to examine the assertion (*1*) that water formed during the titration is strongly held by the platinum black and will not desorb in the absence of a hydrophilic support.

EXPERIMENTAL METHODS

The volumetric measurements were made on an apparatus identical to that described previously (*15*) except for the addition of a second liquid nitrogen trap between the pump and the sample. This apparatus, in which a nominal vacuum of 10^{-6} torr was attained, was also used to measure the BET surface areas to conduct the hydrogen–deuterium exchange reaction.

Preliminary experiments indicated that neither the extent of hydrogen adsorption nor the hydrogen–oxygen reaction were affected by replacing hydrogen by deuterium. Consequently the two isotopes could be interchanged, and gravimetric measurements became feasible.

A Cahn RG 2000 electrobalance in a high-vacuum system was used for the gravimetric measurements. Full details of this apparatus are given elsewhere (*20*). With samples weighing about 150 mg and an ambient pressure of 50 torr, the microbalance would easily detect weight changes of one μg.

Liquid Carbonic hydrogen (99.5%) and Matheson deuterium (99.5%) were purified by passage through a Milton Roy Company palladium thimble purifier. Liquid Carbonic oxygen (99.5%), Liquid Carbonic nitrogen (99.99%), used for the BET measurements, and Matheson helium (99.995%), used for dead space measurements, were passed through liquid nitrogen cold traps before use.

Platinum black from Engelhard Industries, Inc., lot no. 10272, was used in all the experiments. A typical elemental analysis obtained from Engelhard for a platinum black is given in Table 4. Engelhard reported that their platinum black is usually about 99.97% pure. Since Sandler and Durigon (*16*) report that carbon may seriously alter the adsorptive properties of platinum samples with low surface area, we had our sample of platinum black analyzed for carbon; carbon could not be detected and is therefore present at levels below 300 ppm, the detection limit of the analytical method used. A conservative calculation shows that 1000 ppm (or 0.1%) of impurities of atomic weight 100 will cover only about 5% of the surface of our platinum black (about 10 m^2/g) even if all of the impurity atoms accumulate at the surface.

TABLE 4
TYPICAL IMPURITIES (ppm) OF PLATINUM BLACK (99.97% pure)

C	<300
Na	<100
Pd	40–50
Au	20–30
Rh	~20
Fe	20–40
Si	~40
Al	<50
Sn	<20
Ca	~15
Ir, Ag, Cu	Each ~ 10
Ru, Os, Zn, Mg	Each < 10
Ni, Cr, Mn, B, Co	Each < 5
Sb, As, Bi, Cd, Mo, Te	Not detectable

The initial pretreatment of the platinum black consisted of evacuation at room temperature for 30 min and at 125°C for 30 min; the sample was then very slowly exposed to hydrogen or deuterium at room temperature for 1 hr and at 125°C for 30 min and was then outgassed at 125°C for 16 hr before cooling *in vacuo* to room temperature.

It was not necessary to repeat this long initial pretreatment after each adsorption run to reproduce the original surface. Therefore, a shorter, equally effective pretreatment was employed for the runs following the first uptake. After every hydrogen or deuterium adsorption or titration the sample was outgassed 1–2 hr at room temperature and 16 hr at 110–120°C. Gravimetric measurements after an oxygen uptake showed that the platinum black reached a stable weight after about 2 hr of evacuation at room temperature. After an oxygen uptake, the samples were evacuated at room temperature for at least 6 hr to remove adsorbed water prior to titration with hydrogen or deuterium.

After the longer initial pretreatment the amount of hydrogen remaining on the platinum surface was determined by exchange with deuterium in a manner similar to that of Hall and Lutinski (*3*) and Hightower and Kemball (*21*). A large excess of hydrogen was admitted to the sample after pretreatment with deuterium in the volumetric system. The gas was then mixed continuously over the platinum for 2 hr at room temperature by varying the pressure in the system. A portion of the resulting gas mixture was then removed for gas chromatographic analysis (*22*).

Baths of liquid nitrogen, Dry Ice–acetone and chloroform slurry gave temperatures close to −196, −80, and −60°C, respectively. A thermocouple in contact with the adsorption chamber was placed in the bath to record the temperature of each run.

For adsorption measurements a rigorous experimental procedure was followed. The low-temperature baths were placed around the sample 60 min before the introduction of the adsorbate. Low-temperature isotherms were measured 30 min after the introduction of the adsorbate.

The room-temperature isotherms were recorded 60 min after the removal of the baths. All gases were leaked into the evacuated and cooled chamber as slowly as possible to minimize surface heating. This avoided sintering and allowed us to obtain reproducible results on a single sample.

RESULTS

Volumetric Data

All BET adsorption isotherms were obtained in the volumetric system, and surface areas were calculated with a cross-sectional are of 16.2 Å^2/nitrogen molecule.

Oxygen and hydrogen adsorption isotherms are shown in Fig. 1. These data are uncorrected for residual hydrogen on platinum black prior to the adsorption run. They were obtained at room temperature (RT) and low temperature (LT) in the range between −60 and −80°C. The oxygen isotherms are almost flat, but the hydrogen isotherms curve down at low pressures. All stoichiometric ratios reported in Table 5 are those corresponding to an arbitrarily chosen pressure of 50 torr, a value that was used consistently in the gravimetric work. All values of x and y reported in Table 5 and calculated on the basis of 1.19×10^{15} sites/cm^2 have been corrected for slightly variable BET surface areas, as shown, and for residual hydrogen remain-

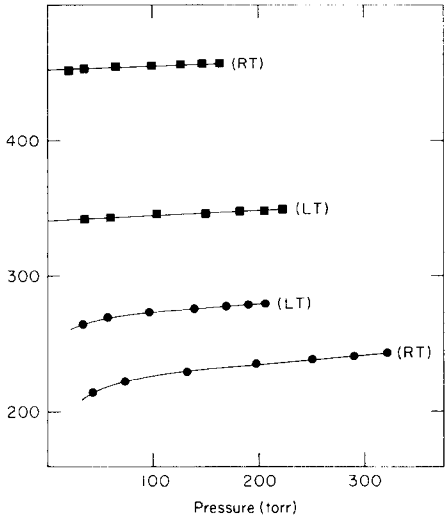

FIG. 1. Oxygen (■) and hydrogen (●) uptakes (μmole) on Pt black (4.67 g); data uncorrected for residual hydrogen.

TABLE 5
STOICHIOMETRIC RATIOS DETERMINED VOLUMETRICALLY

Sample	Run	y LT	y RT	x RT	$2[x + (z/2)]$ LT	$2[x + (z/2)]$ RT	BET surface area (m^2/g)
A	1	0.97	0.87				11.5
	4[a]	0.98	0.84				—
	6[a]			0.84			—
	7				2.64	2.49	9.9
	8	0.98	0.87				10.1
	9			0.84			—
	10				2.65	2.52	8.9
	11			0.83			9.6
B	1			0.84			6.6
	2					2.52	—
	3			0.82			5.3
	4					2.58	—
	5			0.85			5.8
	6					2.55	—
	7			0.85			5.2
		0.98 + 0.01	0.86 + 0.02	0.84 + 0.01	2.65 + 0.05	2.53 + 0.03	

[a] Runs 2, 3, and 5 with sample A were conducted after evacuation periods other than that of the standard pretreatment.

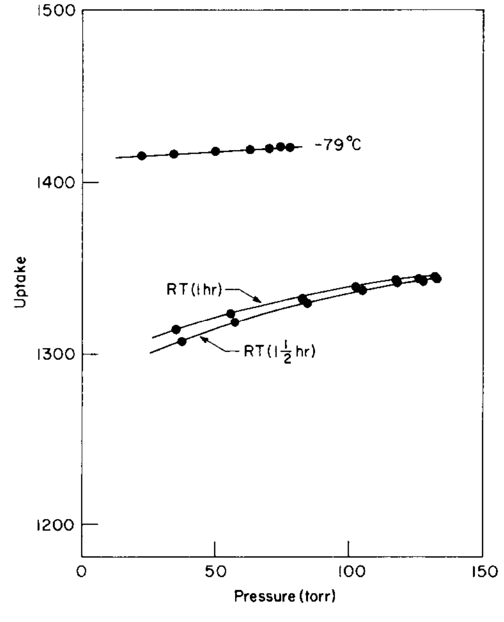

FIG. 2. Desorption of hydrogen following titration at −79°C and warm-up to room temperature: uptake (μmole) on Pt black (4.67 g).

ing on the surface after the outgassing schedule followed in our pretreatment. This amount of residual hydrogen was determined by hydrogen–deuterium exchange to be equivalent to $y = 0.4$. Finally, following a titration at low temperature, adsorption data were measured at higher temperature as shown in Fig. 2.

Gravimetric Data

A recorder tracing showing the weight change during a hydrogen titration initiated at liquid nitrogen temperature followed by warm-up to room temperature is shown in Fig. 3. Another tracing (Fig. 4) shows the weight history of a sample during titration conducted entirely at —62°C, followed by warm-up to room temperature. Reproducibility of the data was very good. Thus, after a 24 hr period, which included a D_2 uptake and a 16-hr outgas at 120°C, the gravimetric trace returned to a zero position identical to that noted before the beginning of the uptake run. This indicated no measurable surface contamination during this period. All gravimetric data are collected in Table 6. Values of x and y in Table 6 were calculated in the same manner as those collected in Table 5. There is excellent agreement between the arithmetic average values of data reported in Tables 5 and 6 together with their 90% confidence

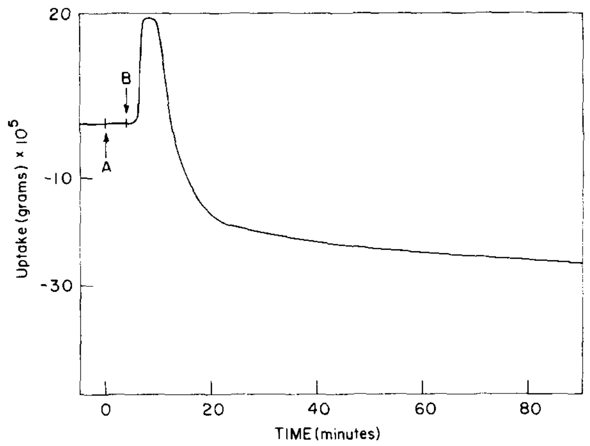

FIG. 3. Gravimetric titration on Pt black (0.164 g): A, introduction of D_2 at −195°C; B, removal of liquid nitrogen bath.

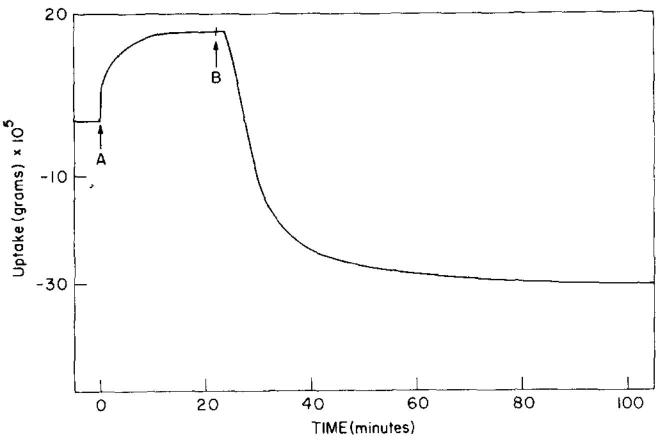

FIG. 4. Gravimetric titration on Pt black (0.166 g): A, introduction of D_2 at −62°C; B, removal of $CHCl_3$ bath.

TABLE 6
STOICHIOMETRIC RATIOS DETERMINED GRAVIMETRICALLY

RT		$2[x + (z/2)]$ LT
y	x	
1.02	0.86	2.01
0.94	0.83	2.42
0.82	0.84	2.54
0.76	0.74	2.34
0.84	0.81	2.22
	0.88	3.34
	0.82	2.57
	0.84	2.54
0.88 ± 0.10	0.83 ± 0.03	2.50 ± 0.26

limits given at the bottom of the tables. This agreement is remarkable since the ratio of total platinum surface area to system volume was nearly three orders of magnitude smaller in the gravimetric system than in the volumetric system. The self-consistency of all data gives additional support to the idea that there was no surface contamination of the samples in the balance apparatus.

DISCUSSION

The main question raised in the present work is the following: what happens to water formed during a titration on platinum according to Eq. (3)? If water leaves the surface, as indicated in this equation, is additional hydrogen taken up by the liberated surface sites? More quantitatively, is the value of the stoichiometric ratio y, pertaining to adsorption of hydrogen at a given temperature and pressure, identical to the value of the stoichiometric ratio z, pertaining to a titration performed under the same conditions? We shall first discuss these questions qualitatively and then quantitatively. Finally, we will discuss our x, y, and z values and compare them to those found in Tables 1 to 3.

Let us first consider *qualitatively* the problem of water adsorption in the presence of hydrogen. The behavior of water on platinum has not been studied extensively. Chon *et al.* (*18*) and Tomezsko and Furukawa (*23*) reported that water desorbs almost completely from unsupported platinum following titrations at 0 and 7°C, respectively. However, it has been proposed that in the absence of a hydrophilic support water will not desorb from platinum (*1*). That water does, in fact, desorb readily at room temperature is clearly evident from the microbalance recorder traces shown in Figs. 3 and 4. In the experiment shown in Fig. 3, the oxygen-covered and evacuated platinum sample was cooled to —196°C and exposed to deuterium at point A. The liquid nitrogen bath was removed at point B and the sample left to reach room temperature. The trace peak height corresponds to a $2[x + (z/2)]$ value of 2.42 while the weight loss after 80 min of desorption corresponds to a loss of 73% of the water formed during titration.

It may be objected that the loss of water was caused by surface heating as a result of the titration. In an attempt to keep the surface temperature under control during the titration, a chloroform slurry was maintained around the adsorbent chamber. The gravimetric course of the titration is shown in Fig. 4. Upon removal of the bath at point B, *water quickly left the surface* with nearly 80% of the total amount of water formed desorbing in 90 min.

This rapid desorption of water from the platinum surface was repeated under slightly different conditions. It was found to occur both in the presence and in the absence of a water trap such as a zeolite or liquid nitrogen trap. However, the large glass surface area of the balance chamber would be expected to act as a trap for the water.

The next question is to decide whether hydrogen readsorbs as water leaves the platinum surface following a titration. The volumetric data provide a decisive negative answer to this question. Titration at —79°C, followed by warming to room temperature, resulted in a *net decrease* of adsorbed gas as shown in Fig. 2. A titration at —62°C gave similar results. A liquid nitrogen cold finger placed close to the adsorption bulk collected the desorbing water. Although frozen water was visible in the cold finger, no quantitative evaluation was possible due to large amounts of water apparently adsorbed on the glass walls of the system. Titrations with dehydrated alumina added in lieu of a cold finger gave adsorption–desorption results identical to those shown in Fig. 2.

From a *quantitative* standpoint, we will focus our attention on the volumetric data collected in Table 5. Because of the difficulty in making good gravimetric measurements with a light molecule, the gravimetric results of Table 6 will not be discussed any further, except to say that they are in good agreement with the volumetric data. From all the data in Table 5 we obtain $x = 0.84 \pm 0.01$, $y = 0.86 \pm 0.02$ and $z = 0.85 \pm 0.05$. Within experimental error, the values of y and z are equal under identical conditions of temperature and pressure. Thus at room temperature and 50 torr pressure, water is displaced from the surface by hydrogen, as first suggested by Chon *et al.* (*18*). The amount of hydrogen adsorbed on platinum is the same in adsorption and titration. Furthermore, within experimental error, the amounts of oxygen adsorbed, hydrogen adsorbed and hydrogen consumed in a titration are in the ratio 1:1:3.

Finally, it is of interest to compare values of x, y, and z listed above with those reported by other investigators. First of all, it is necessary to specify the conditions of adsorption. Indeed, as shown in Fig. 1, the hydrogen isotherms exhibit a drop-off at low pressures, and there is a slight increase in uptake with pressure at the higher values of pressure investigated. The pressure and temperature dependence of hydrogen adsorption indicates a weak form of chemisorption of hydrogen on platinum at higher values of y. This is in agreement with calorimetric (*18*, *23*), conductimetric (*24*, *25*) and surface potential measurements (*26*). By contrast, oxygen isotherms were very flat (Fig. 1), and it was not possible to remove oxygen by pumping at room temperature.

Thus we expect to find higher values of y at temperatures below room temperature and at pressures above 50 torr. In this work we have observed values of y close to unity at low temperature and 50 torr (see Table 5). At low temperatures and at a pressure of 1 atm, we have measured values of y as high as 1.05 to 1.10. But we have not observed values of y in the vicinity of two. Such a value has not been reported (see Table 1) but has been suggested by others (*1*). That suggestion originated in older work by Benton (*2*), who did not have BET surface areas at his disposal, did not measure residual hydrogen *directly* and used a system where poisoning of the surface by mercury was a serious possibility.

In our work, correction for residual hydrogen has been made. As stated earlier, nearly 40% of the platinum surface atoms remained covered with deuterium or hydrogen after our pretreatment. This compares favorably with observations of Boreskov and Vasilevich (*8*) and Piringer and Tataru (*27*). The first pair of investigators found that 30% of the hydrogen adsorbed on a platinum film could not be removed by evacuation at 150°C. Piringer and Tataru found that an average of 29% of the hydrogen adsorbed on a platinum powder was desorbed at 25°C. With respect to oxygen adsorption, too high values of x may be due to the failure to correct for residual hydrogen (*15*). Mears and Hansford have recently stressed the importance of such a correction (*1*).

Finally it must be stressed that we attach no significance to the near equality of x and y values reported in Table 5. As discussed above, the value of y depends on temperature and pressure. From the present work and that of others (Table 2), it appears that for oxygen x is somewhat less than unity. Further work must decide whether this is due to the fact that oxygen forms an immobile layer with holes in it (*28*) or to an improper assumption of site density necessary for the calculation of stoichiometric ratios. The proper site density depends on the nature of exposed crystallographic planes. That open planes such as the (*110*) face are exposed is suggested by the fact that values of y are greater than those of x at higher pressures and lower temperatures. Indeed, on rough faces like (*110*) there are recessed sites which are not counted in the calculation of site density and are certainly not accessible to oxygen but may be able to bind hydrogen in a rather weak adsorbed state.

CONCLUSION

The combined use of gravimetric and volumetric techniques has succeeded in showing that the water formed in the reaction of hydrogen with oxygen adsorbed on platinum black leaves the surface at room temperature and does not interfere with the adsorption of hydrogen. This result confirms in every point the conclusion reached by Aston and co-workers (*18*). The stoichiometric ratio of adsorbed hydrogen is the same, under identical conditions of temperature and pressure, after adsorption on a reduced or an oxidized platinum surface. In spite of non-integral values of x and y, as well as a value of x slightly smaller than unity and a value of y slightly dependent on pressure and temperature, an excellent approximation to the stoichiometry found in this work remains the same as that used earlier by ourselves and by others (*15*, *18*):

$$Pt_s - O + 1.5H_2 \rightarrow Pt_s - H + H_2O$$

The remaining uncertainty in the stoichiometry of this titration is ascribed principally to the uncertainty in the surface density of platinum atoms.

ACKNOWLEDGMENTS

This work has been supported by grants from Esso Research and Engineering Company and the National Science Foundation (GK 2208).

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