

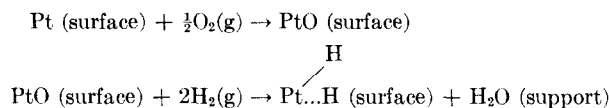
## The Stoichiometry for Hydrogen Titration of Oxygen on Supported Platinum

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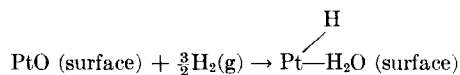
Received May 26, 1967

A reinvestigation of the reaction between hydrogen and oxygen chemisorbed on supported platinum has established the following stoichiometry for conditions of 25°C and pressures above about 10 torr:



This represents a significant revision of previously suggested chemistry requiring titration uptakes of two or three hydrogen atoms per surface platinum atom supported on hydrophilic oxides. The new stoichiometry is consistent with considerable evidence that hydrogen adsorption on a clean Pt surface occurs with both strongly and weakly bound species, and that H/Pt ratios approach 2 under the above conditions.

With unsupported platinum, a different stoichiometry for the hydrogen titration prevails, namely,



This is attributed to the relatively strong bonding of water to platinum in the absence of a hydrophilic support. The second hydrogen atom, being more weakly adsorbed than the first, is unable to displace adsorbed water.

Use has been made of the revised stoichiometry for supported platinum in determining the dispersion of platinum on alumina and platinum on silica. A new flow method for routinely performing the hydrogen titration of chemisorbed oxygen is described. Results by this method compare favorably with those obtained with a more precise (but more tedious) static method.

### INTRODUCTION

The most important parameter affecting the hydrogenation or dehydrogenation function of supported platinum (or other metal) catalysts is undoubtedly the available metal surface. For a given metal content, the ratio of exposed to total metal atoms can vary markedly with preparation and pre-treatment conditions. In addition, under certain conditions of use, agglomeration of originally dispersed metal particles may occur, leading to serious loss in catalytic

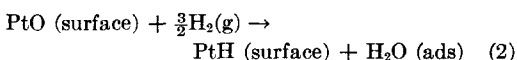
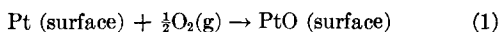
activity. Both in the development of improved catalysts and in the optimization of their commercial use, rigorous methods for following changes in metal dispersion are required.

The dispersion of platinum on alumina and other supports has been extensively studied by both physical and surface chemistry methods. Physical techniques (1-3), while often convenient experimentally, generally do not provide useful information in the range of metal particle sizes

which are of greatest interest to the catalytic chemist. Surface chemistry methods, such as selective chemisorption (4-11), surface titrations (12-15), and hydrogen-deuterium exchange (16), provide more useful information because they sense the intensive and extensive properties of the surface rather than bulk properties such as particle size and shape. However, these methods generally lack sensitivity in dilute systems, involve ill-defined stoichiometry, or require tedious high-vacuum techniques.

The hydrogen titration of oxygen chemisorbed on platinum surfaces appears to offer one of the best approaches to the problem. Such a method was implicitly suggested by Gruber (8), who proposed various reaction schemes involving platinum, hydrogen, and oxygen. However, at the high temperature (350°C) used by Gruber, bulk oxidation of platinum occurs, thus limiting the method to highly dispersed systems. Benson and Boudart (14) recognized that the hydrogen-oxygen titration offers a means of multiplying the sensitivity of direct hydrogen adsorption measurement. By adsorbing oxygen at room temperature, the problem of bulk oxidation of large platinum particles is eliminated, and the water formed by the titration at this temperature is scavenged by hydrophilic supports such as alumina and silica. They also showed that hydrogen and oxygen adsorption isotherms for platinum on alumina are parallel to those measured on the platinum-free support. Thus, the uptake by exposed metal atoms is obtained directly by extrapolation to zero pressure. This eliminates the need for a blank determination on the metal-free support, which is rarely available in the case of commercial catalysts.

Benson and Boudart adopted the stoichiometry suggested by Gruber (8) and by Chon *et al.* (15):



They determined the stoichiometry for a 1.96% platinum-on-alumina catalyst, and

obtained a ratio of 3.2 for the hydrogen titration to oxygen adsorption uptakes. Thus, *under their experimental conditions* the above stoichiometry seemed to be verified.

There appears to be considerable disagreement among other workers regarding the stoichiometry of these reactions. Weidenbach and Fürst (12) and Jaworska-Galas and Wrzyszczyk (13), using flow methods for the titration of supported platinum, apparently employed a different stoichiometry in their work. Thus, they seem to have neglected the additional adsorption of hydrogen on the reduced metal resulting from the titration of adsorbed oxygen. Furthermore, some investigators (21-23) have shown that hydrogen-platinum ratios as high as 2 can result under certain experimental conditions.

In view of these uncertainties, we have reinvestigated the stoichiometry on a series of supported platinum catalysts using a conventional static volumetric system and a more rapid flow system.

#### EXPERIMENTAL

The flow chemisorption method was designed primarily for routine measurement of metal dispersion. Although similar in principle to other dynamic adsorption techniques (9-13), the current approach has certain advantages over slug-flow methods. The continuous titration with dilute hydrogen is simple to do, requiring only a constant flow of titrant during the measurement. No complicated dosing measurements or pre-estimate of slug size are required. The very rapid reaction between hydrogen and adsorbed oxygen results in a sharp breakthrough of hydrogen which is easy to detect with a simple thermal conductivity cell. Although a blank run is required to cancel out the effect of dead volume, this measurement is made on precisely the same sample as used in the titration and therefore cancels out any adsorption on the support. The method, of course, has all the advantages of other flow methods, such as elimination of vacuum systems, mercury vapor, and other common contaminants.

The flow apparatus, shown schematically

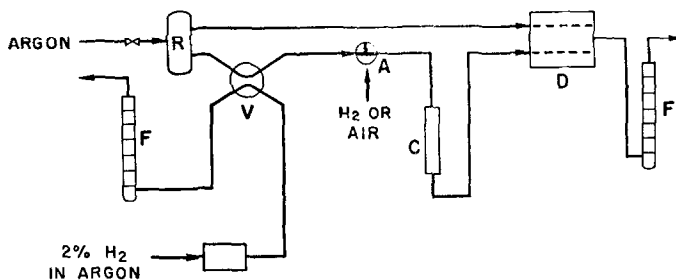


FIG. 1. Schematic drawing of flow apparatus.

in Fig. 1, is assembled from readily available hardware used in chromatographic studies. The adsorption cell (C), measuring 6 or 10 mm OD by 15 cm, holds catalyst samples of 7 to 20 g. Following catalyst pretreatment (described later), an argon flow is established through the catalyst. This stream and a 2% H<sub>2</sub> in argon stream are each regulated at 25 cc/min by a Milliflow dual back-reference controller (R) and a Moore constant-differential flow controller (S), respectively. Flow rates are measured with soap-film flow meters (F).

To measure hydrogen adsorption, the flow is switched from argon to the 2% H<sub>2</sub>-Ar mixture by means of the four-way valve (V). The stream composition is monitored by a Gow-Mac gas-density indicator (D), but a thermal conductivity cell would serve equally well. A Bristol Dynamaster (1 mV) recorder registers the time required for breakthrough of the hydrogen, typically 10 to 20 min. Since the corners of this step-change are rounded somewhat by diffusion, the time elapsed is taken as the time to the midpoint. Argon purging for 15 min follows, to remove reversibly adsorbed hydrogen from the support. Next the flow is again switched to H<sub>2</sub>-Ar to determine dead volume plus support adsorption. Breakthrough in this measurement generally occurs in 3 to 4 min. The difference in time for the two steps represents hydrogen taken up on the metal alone.

The hydrogen uptake  $U$ , in  $\mu\text{moles/g}$ , is calculated from the expression

$$U = \frac{0.0234f(t_c - t_a)}{W} \left[ \frac{273}{T_a} \right] \left[ \frac{P_a}{760} \right] \frac{10^6}{22\,414}$$

in which  $f$  is the flow rate of the H<sub>2</sub>-Ar mixture,  $(t_c - t_a)$  is the difference in breakthrough time,  $W$  is the catalyst weight (dry basis), and  $P_a$  and  $T_a$  are ambient pressure and temperature. The factor 0.0234 is the mole fraction of hydrogen in the H<sub>2</sub>-Ar mixture. This was determined by combustion of the H<sub>2</sub>-Ar mixture over CuO at 500°C, and collection of the product water in silica gel traps. The factors 22 414 cc/mole and  $10^6 \mu\text{moles/mole}$  merely convert the uptake from cc-(STP)/g to  $\mu\text{moles/g}$ .

The static apparatus was similar to that used by Benson and Boudart (14). Adsorbents were protected from mercury vapor by a small trap filled with gold powder in early runs, and by a cold finger at liquid nitrogen or Dry Ice temperature in later runs. Auxiliary equipment included a gas purification train, and a mercury diffusion pump isolated from the adsorption apparatus by a zeolite trap at liquid nitrogen temperature.

Catalysts used in this study include both alumina- and silica-supported low-platinum contacts, whose properties are summarized in Table 1. The alumina-supported samples (A-F) are typical commercial catalysts, which are charged in the as-received, pelleted or extruded form. Catalysts G-J are experimental catalysts. The support for Catalyst G was prepared by ammoniacal hydrolysis of (EtO)<sub>4</sub>Si (Eastman practical grade) at a pH of 10, followed by drying for 6 hr at 110°C. The support for Catalyst H is a commercial silica gel (Davison PA 400) which was soaked in 1 N NH<sub>4</sub>OH for 65 hr before loading with platinum. Cata-

lyst J is based on eta alumina prepared from high-purity bayerite (Morton Chemical Co.) by pelleting with 2% Sterotex (hydrogenated corn oil), granulation to 10–20 mesh particles, and calcination in air for 12 hr at 400°C. The calcined alumina was soaked in 1 N NH<sub>4</sub>OH for about 5

TABLE I  
CATALYST PROPERTIES

Catalyst	Wt % Pt	Support	Surface area, (m <sup>2</sup> /g)
A	0.36	Alumina	164
B	0.56	Alumina	182
C	0.45	Alumina	191
D	0.33	Alumina	413
E	0.57	Alumina	269
F	0.71	Alumina	145
G	0.97	Silica	314
H	0.93	Silica	377
J	0.77	Alumina	307

hr before loading. The platinum was exchanged at 25°C into these granular supports with ammoniacal platinum tetramine dichloride at a pH of 10 over a period of 20 or more hours. Catalysts G–J were dried in flowing air at 60°C for several hours (110°C for Catalyst J), and in flowing argon at 150°C for 16 hr before reduction.

Tank hydrogen, helium, and argon were obtained from the American Cryogenics Company. The hydrogen was purified by passage through a bed of palladium Deoxo catalyst and zeolite drying agent. Helium was used for dead volume measurement after passage through a reduced copper oxide at 400°C, and a liquid nitrogen trap. The argon for dynamic outgassing passed through a similar copper trap at 400°C. Oxygen was prepared by thermal decomposition of thoroughly outgassed potassium permanganate, and purified by passage through a KOH trap and a zeolite drying agent.

In both the flow and the static methods, pretreatment of the catalyst is done *in situ*. Outgassing is accomplished by means of evacuation in the static apparatus, and by dynamic outgassing with purified flowing argon in the flow apparatus. Following

outgassing for 15–20 min at room temperature, the catalyst cell is surrounded by a cold furnace and heated to 150°C. Outgassing is continued for 1–2 hr at this temperature before starting reduction with flowing hydrogen at 100 cc/min. After raising the temperature to 500°C over a period of 2 to 3 hr, the hydrogen treatment is continued for 2 hr. However, a reduction temperature of 300°C was used with catalyst G to minimize sintering (21). Each catalyst is outgassed overnight (16 hr) at 500°C to obtain a clean surface for oxygen or hydrogen adsorption, and then rapidly cooled to the desired adsorption temperature. If only a titration of adsorbed oxygen is desired, a short outgassing at 500°C is sufficient. In this case, any hydrogen remaining on the metal surface is reacted away when oxygen is introduced at room temperature. Following adsorption of oxygen, the catalyst is outgassed for 1 hr before starting a titration measurement.

## RESULTS

To obtain more precise information on the stoichiometry of the titration, isotherms were determined statically for hydrogen and oxygen adsorption on the clean metal surface, and for hydrogen titration of oxygen chemisorbed on the platinum. A typical set of measurements for Catalyst F, shown on Fig. 2, exhibits a decrease in the slope of the isotherms following each pretreatment. The sorption capability of this support apparently decreases after each high-temperature treatment. However, the intercepts, which give net adsorption by the metal, are quite reproducible. The net uptakes for hydrogen titration, hydrogen adsorption and oxygen adsorption on the series of catalysts were generally found (see Table 2) to be in a ratio of 4:2:1.

The number of exposed metal atoms is calculated from the titration uptakes, following the stoichiometry discussed in the next section. To quantitatively describe metal dispersion, it is convenient to define a dispersion ratio, *D*, as the ratio of exposed to total metal atoms. Since this ratio is physically meaningful in itself, it is unnecessary to convert it to a metal surface

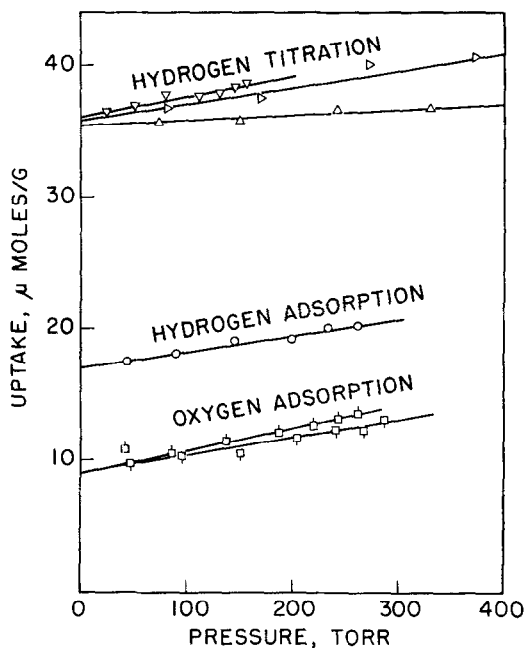


FIG. 2. Adsorption and titration isotherms for Catalyst F.

area. The calculated dispersion ratios are presented in the last column of Table 2.

The dynamic apparatus was next used to measure the hydrogen titrations, and in a

few cases hydrogen adsorption, on this series of catalysts. The same catalyst sample was often used, although fresh samples were charged to each apparatus in several cases. With the flow apparatus, a hydrogen titration can be measured and calculated in about 45 min, while over 3 hr is required with the static apparatus. Table 2 shows that the results obtained with each method are in fairly good agreement.

Titration results with either method are reproducible, provided that the pretreatment procedure is adhered to. However, inconsistent results were obtained with samples which had been stored for 6 to 7-months following titration measurements. Higher uptakes can occur due to a slow, partial bulk oxidation during storage, while lower uptakes can result from adsorption of water on the support, or contamination of the metal surface. When each stored sample was again pretreated, the correct uptakes were obtained.

## DISCUSSION

The difficulty in establishing the stoichiometry of adsorption on typical supported

TABLE 2  
SUMMARY OF UPTAKE DATA

Catalyst	Pt content		Uptakes (μmoles/g)					Ratio of H <sub>2</sub> titration to O <sub>2</sub> ads.	Dispersion ratio <sup>a</sup>
	wt %	μatoms/g	Flow method		Static method				
			H <sub>2</sub> ads.	Titration	Titration	H <sub>2</sub> ads.	O <sub>2</sub> ads.		
A	0.36	18.4	—	11.8	12.2	—	3.1	4.0	0.33
					11.8			3.8	
B	0.56	28.7	—	14.1	14.6	—	3.9	3.7	0.25
C	0.45	23.1	8.4	13.7	15.8	7.9	—	—	—
			7.5	—	15.4	7.8	3.4	4.5	0.33
D	0.33	16.9	—	10.1	9.8	—	2.4	4.1	0.29
E	0.57	29.2	—	14.9	13.2	—	3.9	3.4	0.23
			—	15.3	—	—	—	3.9	—
F	0.71	36.7	16.2	28.1	36.2	—	9.0	4.0	0.49
			—	28.9	35.8	17.0	9.0	4.0	—
G	0.97	49.7	11.8	28.1	25.2	12.0	—	—	0.25
			12.0	—	—	—	—	—	—
H	0.93	47.6	—	43.7	45.2	24.5	11.2	4.0	0.47
			—	—	45.2	—	11.2	4.0	—
J	0.77	39.5	10.0	18.7	19.8	10.0	5.0	4.0	0.25

<sup>a</sup> From static measurements.

metals is that, initially, both the detailed chemistry and the dispersion are unknown. A common early approach was to calibrate hydrogen uptakes on metal blacks or films, using the crystallographic site density and surface areas measured by the BET method. Recently, several workers (21, 22) have demonstrated that supported platinum catalysts with dispersion ratios of 1 can be prepared via ion exchange. Chemisorption studies on such catalysts provide more direct information on the stoichiometry. Before discussing our titration results, it is instructive to review the available information for hydrogen adsorption on both unsupported and supported platinum.

### Hydrogen Adsorption

**Unsupported platinum.** Published evidence is sufficient to elucidate the stoichiometry at saturation over a wide range of temperature and pressure. Using a Pt black reduced at 500°C, Spenadel and Boudart (5) calculated a H/Pt (surface) ratio of 0.98 for hydrogen chemisorption at 250°C and 250 torr. However, at 25°C and 1 atm, Benton (18) observed the following uptakes on a platinum black which had been stabilized by repeated cycles of oxidation and reduction:

Gas	H <sub>2</sub>	CO	O <sub>2</sub>
Uptake (vol/vol Pt)	36.7	37.8	20.4

There is ample evidence (12, 14, 15) that oxygen at these conditions is dissociatively adsorbed with one oxygen atom per exposed platinum atom, and that CO is linearly bound on unsupported Pt (10, 29). Thus, assuming O/Pt and CO/Pt ratios of 1, Benton's results suggest that the H/Pt ratio approaches 2 at 25°C and 1 atm.

Published isobars (4, 18-20) for hydrogen adsorption on unsupported platinum generally show two branches below 0°C. Starting at -196°C, the observed hydrogen uptakes increase to a peak value at 20° to 40°C, and then decrease steadily on heating to 250°C. Upon cooling, this isobar is reversible to about 20°C. Then instead of decreasing along the lower branch, the up-

take remains nearly constant to -196°C, forming an upper branch. For comparison purposes, these hydrogen isobars were converted to H/Pt ratios by normalizing the maximum uptake to a value of 2.0. Figure 3 shows the resulting 200 torr isobar to

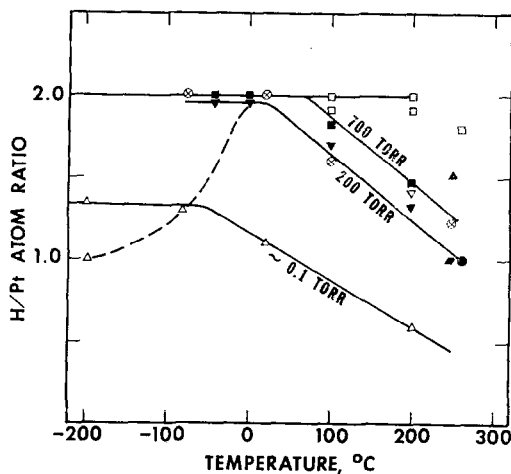


FIG. 3. Dependence of hydrogen to platinum atom ratios on temperature and pressure. Dotted line gives locus of activated adsorption. *Unsupported metals, H/(Surface Pt)*:  $\blacktriangledown$ , 200 torr, Sievert and Brüning;  $\blacksquare$ , 700 torr, Sievert and Brüning;  $\bullet$ , 200 torr, Boreskov and Karnaukov;  $\blacktriangle$ , 640 torr, Boreskov and Karnaukov;  $\blacklozenge$ , 240 torr, Spenadel and Boudart. *Supported Metals, H/(Total Pt)*:  $\nabla$ , 200 torr, 20 hr, Rabo *et al.*;  $\square$ , 600 torr, 20 hr, Rabo *et al.*;  $\otimes$ , 50-200 torr, present work;  $\triangle$ ,  $\sim$ 0.1 torr, Poltorak and Boronin.

have a value 1 at 260°C, in good agreement with the finding of Spenadel and Boudart at 250°C. More recently, Kavtaradze (23) found the same behavior of isobars on evaporated metal films. By comparison with the krypton BET surface area, the peak value was shown to correspond to two hydrogen atoms per platinum atom.

**Supported platinum.** Poltorak and Boronin (21) reported an isobar of similar form (see Fig. 3) obtained on silica-supported platinum, prepared by cation exchange with platinum tetrammine dichloride. The lower-branch isotherm, measured at -196°C and 0.1 to 0.7 torr, gives H/Pt (total) ratios of exactly 1.0 when extrapolated to the intercept. The isotherm for hydrogen chemisorption at -196°C reaches saturation at

pressures as low as  $10^{-5}$  torr, showing a fast, nonactivated adsorption. On increasing the temperature, the 0.1 torr isobar passes through a peak of  $H/Pt = 1.3$  before decreasing like the higher pressure isobars. The upper branch is reproducible, provided the temperature is kept below  $400^{\circ}C$ , but it is possible to return to the lower branch by outgassing at high temperatures.

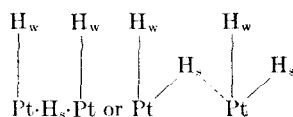
Rabo *et al.* (22) investigated hydrogen adsorption on zeolite-supported platinum, also introduced by cation exchange with platinum tetrammine dichloride. At  $100^{\circ}C$  and 660 torr, they observed a  $H/Pt$  ratio of 2, which was cited as evidence for atomic dispersion. When the temperature was raised to  $200^{\circ}C$ , hydrogen rapidly desorbed to a  $H/Pt$  ratio of 1.4, but then slowly re-adsorbed to a value of 2 after 24 hr. However, with an initial pressure of 200 torr at  $200^{\circ}C$ , the  $H/Pt$  ratio approached a value of 1.4 at equilibrium. Hence, with the exception of values attained after several days at 1 atm and  $200-250^{\circ}C$ , there is general agreement with the plots of Fig. 3.

For freshly prepared alumina-supported platinum, several workers (5, 8) have observed the uptake of one hydrogen atom per platinum atom at conditions of  $250^{\circ}C$  and 250 torr. On the basis of the rapid uptake, Spenadel and Boudart (5) argued that the platinum must exist in monolayer patches or in small crystallites. In our current work, a few isotherms were obtained on Catalyst F at  $-78^{\circ}$ ,  $25^{\circ}$ ,  $100^{\circ}$ , and  $250^{\circ}C$ . The results, normalized to a  $H/Pt$  ratio of 2 at  $-78^{\circ}C$ , are in good agreement with the isobaric data shown in Fig. 3.

The adsorption behavior reviewed suggests that two types of hydrogen adsorption can occur on platinum, quite independently of the physical state of metal. Two types of hydrogen adsorption have been postulated previously (24-28) to explain the results of other experimental techniques. Mignolet (26) followed the adsorption of hydrogen on evaporated platinum films by surface potential measurements. He found both a strongly bonded form which produces a negative surface potential, and a

weakly bonded form which produces a positive surface potential. This weakly bonded species can be removed by pumping at  $20^{\circ}C$ . His strongly bonded form was attributed to covalently bonded hydrogen atoms, and the weakly bonded form to hydrogen chemisorbed as molecules. He suggested the latter are formed by combination of newly adsorbed atoms with those originally chemisorbed in the strongly bonded form. Suhrmann *et al.* (27) also detected two forms of chemisorbed hydrogen on thin platinum films by measuring the change in resistance and the photoelectric emission as a function of coverage.

Pliskin and Eischens (24) observed the infrared spectra of hydrogen adsorbed on silica-supported platinum at 400 torr and  $-78^{\circ}$  and  $35^{\circ}C$ . The presence of two bands in the spectra suggests the presence of two types of hydrogen adsorption. Since experiments with HD do not support assignment of the weakly bonded form to molecular hydrogen, they conclude that both the strongly and weakly bound forms are due to hydrogen adsorbed as atoms. They visualize the following bonding scheme:

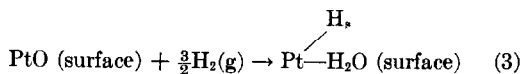


in which the strongly bonded form ( $H_s$ ) is adsorbed over an interstitial position and the weakly bonded form ( $H_w$ ) is adsorbed directly over the platinum atoms. This bonding scheme has since been supported by the detailed theoretical calculations of Toya (25). For alumina-supported platinum Kubokawa *et al.* (28) found heats of adsorption of 21-23 and 9-10 kcal/mole, respectively, for the two types of hydrogen adsorption.

#### Hydrogen-Oxygen Titration

**Unsupported platinum.** Chon *et al.* (15) followed calorimetrically the hydrogen titration of oxygen adsorbed on platinum black. This reaction occurs rapidly at  $25^{\circ}C$ , forming water which remains adsorbed on the metal surface. When additional increments of hydrogen are added, the hydrogen

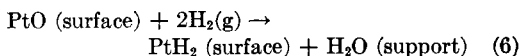
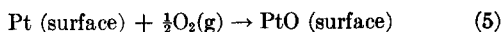
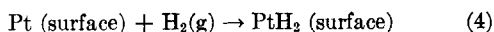
adsorption approaches a monolayer. The overall process can be represented by



In this case, adsorption of water on the platinum appears to inhibit further adsorption of a second weakly bound hydrogen atom. The two-site picture explains their observation that hydrogen adsorption can occur (in the  $\text{H}_s$  position) without displacing the water produced by the reaction.

By desorption experiments, Chon found a value of 11 kcal/mole for the heat of adsorption of water on the metal. In contrast, reported values for the initial heat of adsorption of water on alumina or silica range from 20 to 105 kcal/mole (31-33). The high heats of adsorption indicate a much stronger adsorption of water on either support than on platinum. Thus, with these hydrophilic supports, we would expect water to desorb from the platinum, and readsorb on the support.

**Supported platinum.** The experimental uptake ratios shown in Table 2 indicate that the following stoichiometry prevails on supported platinum at 25°C and hydrogen pressures greater than 10 torr:



This represents a significant revision of the stoichiometry derived in earlier studies of platinum on hydrophilic supports. Thus, a titration uptake of four hydrogen atoms per oxygen atom is required instead of the two or three hydrogens previously suggested.

Our generally consistent values of 4 for the ratio of the net hydrogen titration to net oxygen adsorption are in conflict with a value of 3.2 found by Benson and Boudart (14). This discrepancy probably results from a difference in the outgassing procedure used to obtain a clean surface for oxygen adsorption. After reduction, their catalyst was outgassed for 1 hr at 500°C, while in our work a period of 10 to 16 hr

was used, following Gruber (8) and Spenadel (5). Thus for Catalyst F, several hours were required to achieve a vacuum of  $10^{-5}$  torr, as shown on Fig. 4. The slow outgassing rate is indicative of a slow de-

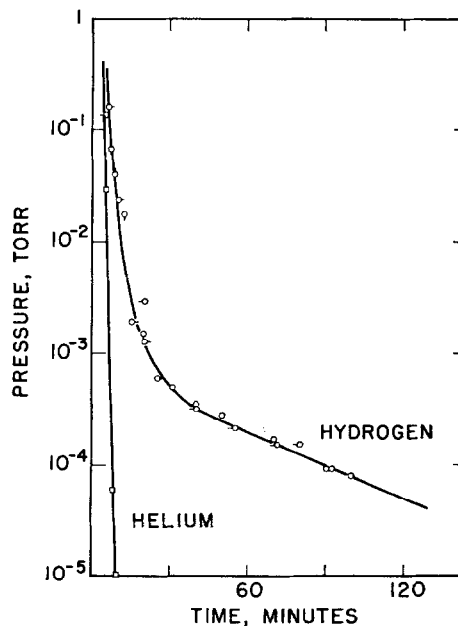


FIG. 4. Times for outgassing hydrogen and helium from Catalyst F:  $\circ$ , hydrogen, catalyst at 500°C;  $\square$ , helium, catalyst at 25°C.

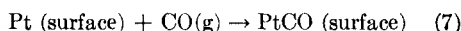
sorption of hydrogen from the platinum surface. In contrast, starting with helium at 1 atm in the cell, the vacuum reached  $10^{-5}$  torr in 10 min. Gruber (8) also states that an outgassing time of at least 6 hr at 500°C is required to obtain a clean surface and reproducible adsorption results. Shorter times can result in incomplete removal of adsorbed hydrogen. Thus, an oxygen adsorption isotherm performed after a 1-hr outgassing may also include an oxygen titration of residual hydrogen atoms.

However, a 1-hr outgassing is sufficient before measuring a hydrogen titration. In this case, oxygen physically bound on the support is easily evacuated to  $10^{-5}$  torr in about 10 min, leaving strongly chemisorbed oxygen on the platinum for the titration step.

Benson and Boudart's interesting comparison of titration uptakes with CO up-



takes, measured by the method of Hughes *et al.* (10), is applicable here as supporting evidence. For a series of platinum-alumina catalysts, a net H<sub>2</sub> to CO uptake ratio of 2 was found over more than a 70-fold range of exposed Pt surface [dispersion ratios of 0.32 to 0.54 calculated by Eq. (6)]. This uptake ratio is exactly what we would predict in comparing Eq. (6) with the following:



which assumes linear bonding. Such bonding is generally accepted (10, 11, 29) to occur at saturation on unsupported or poorly dispersed platinum. At dispersion ratios approaching 1, Gruber (8) found a change in the ratio of CO adsorption to hydrogen adsorption (measured at 250°C). Referring to early infrared studies (29), he postulated that CO is adsorbed in a bridged structure with bonding to two metal atoms. More recently, Blyholder (30) has questioned the existence of a bridge structure, and proposed that the infrared spectra can be explained equally well by linear structures. The excellent agreement of the CO adsorption and hydrogen titration results appears to support Blyholder's position and the stoichiometry proposed in Eq. (6).

#### CONCLUSIONS

Hydrogen chemisorption on platinum in physical states varying from "atomically" dispersed to continuous metal surface has been shown to follow a highly consistent adsorption behavior. The H/exposed Pt ratios may vary from 0 to 2.0 as a function of pressure and temperature. Evidence available from a variety of experimental techniques supports the two-site bonding scheme of Pliskin and Eischens.

For precise measurements of platinum dispersion, the statically determined hydrogen-oxygen titration is recommended. The stoichiometry given in Eq. (6) should be used for platinum supported on hydrophilic supports such as alumina or silica. However with unsupported platinum, the stoichiometry of Eq. (3) applies. The described flow method for hydrogen-oxygen titration appears useful for routine measurements.

#### ACKNOWLEDGMENTS

The authors wish to thank the management of Union Oil Company of California for permission to publish this paper. We also express appreciation for helpful discussions with Prof. T. K. Sherwood, and for assistance by L. L. Sharar in the experimental work.

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