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Chemisorption on Supported Platinum

II. Stoichiometry for Hydrogen, Oxygen and Carbon Monoxide

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The chemisorption of hydrogen, oxygen and carbon monoxide on supported platinum was studied by a pulse technique. Crystallite size was measured independently by electron microscopy. The resulting adsorption stoichiometries were compared with literature data which either include measurements of size or which compare the adsorption of two or more gases on the same solid.

The study confirms that monolayer coverage on supported platinum crystallites corresponds to the adsorption of one hydrogen atom per surface platinum atom ($0.1 < \mathrm{Pt_s/Pt} < 0.9$), within acceptable limits. Most catalysts for which reliable size data are available support this correlation within ±20%.

The stoichiometry of carbon monoxide chemisorption on small platinum crystallites ($\mathrm{H/Pt} > 0.25$) is also reasonably constant. On platinum–silica, carbon monoxide uptakes are typically some 15% less than the corresponding volumes of hydrogen on a molecule/atom basis. Below $\mathrm{H/Pt} = 0.25$, this CO/H ratio declines appreciably, probably due to steric effects. Results for platinum–alumina seem broadly similar, but insufficient data are available for this system.

Volumes of hydrogen and oxygen chemisorbed on supported platinum catalysts vary widely with respect to one another ($0.4 < \mathrm{O/H} < 1.0$). This is probably due to changes in the stoichiometry of oxygen chemisorption on platinum as a result of the thermal history of the sample. Oxygen uptakes substantially lower than those of hydrogen are obtained after reduction for one hour at 500°C, while almost equal volumes of hydrogen and oxygen are adsorbed after 15 hr in hydrogen at 500°C. This phenomenon is largely independent of crystallite size and is tentatively attributed to changes of the platinum surface from a defective form to an equilibrated structure of minimum surface energy.

INTRODUCTION

The stoichiometry of chemisorption on supported metal catalysts may be estimated by extrapolation from pure metal systems. However, theory suggests (*1*, *2*) that small metal crystallites may behave differently from the bulk metal. Even if possible metal–support interactions are neglected, the average coordination number of surface atoms is lower in the small crystallite, and in the limit, essentially every metal atom is a surface atom.

Adsorption properties peculiar to small metal crystallites have been demonstrated by experiment. Van Hardeveld and Van Montfoort (*1*) showed that nitrogen was weakly chemisorbed on 15–70 Å crystallites of several metals which do not normally chemisorb nitrogen. Wilson and Hall (*3*) found the stoichiometry of oxygen chemisorption on platinum–alumina to be variable. Dorling and Moss (*4*) observed similar effects for carbon monoxide chemisorption on platinum–silica.

In contrast, several recent studies suggest that hydrogen chemisorption on platinum yields a reliable measure of surface area if it is assumed that each surface platinum atom adsorbs one hydrogen atom (*3*, *5*, *6*). This singular assumption implies that small platinum crystallites have surface properties identical to those of the bulk metal, which also takes up approximately one hydrogen atom per surface platinum atom (*7*).

The present work examines the stoichiometry of hydrogen, oxygen and carbon monoxide chemisorption on small platinum crystallites. Particular emphasis is placed on independent measurements of platinum crystallite size, and studies incorporating such measurements are reviewed in an attempt to unify the current picture. Some new experiments were designed to test adsorption properties as a function of crystallite size and the methods used to vary size. Since independent measurements of dispersion were essential to these objectives, methods of making these measurements were examined in detail. Electron microscopy was used extensively since many of the samples were not amenable to the X-ray diffraction method. Debye line broadening was also employed for those samples in which platinum crystallite size was sufficiently large.

EXPERIMENTAL

Chemisorption—procedure and definitions. The pulse adsorption method and its utility for the measurement of hydrogen and oxygen chemisorption were discussed previously (*6*). In the present study, a typical experiment involved the following sequence: With 50 cc/min hydrogen flow, catalyst temperature was raised slowly (4°/min) to 500°C and held at this temperature for one hour. The gas flow was then changed to nitrogen (30 cc/min), the temperature maintained at 500°C for one hour and the sample cooled to room temperature. This will be referred to as "standard reduction" throughout. Hydrogen chemisorption (H_A) was then measured. When the final hydrogen pulse was fully eluted, the adsorbed hydrogen was titrated with oxygen to give O_T; and subsequently, the hydrogen–oxygen titer (H_T) was measured. After heating briefly to 500°C in hydrogen and stripping for one hour at the same temperature in helium (30 cc/min), carbon monoxide chemisorption (CO_A) was measured at room temperature. Samples were discarded at this stage since the surface is difficult to clean after the adsorption of carbon monoxide (*3*). For the same reason, an intermediate determination of CO_A was not made if catalysts were to be reexamined after more prolonged periods of reduction.

Oxygen chemisorption (O_A) was calculated as ($O_T - 1/2H_A$), since it was shown previously (*6*) that O_A obtained in this way was equivalent to a direct determination. In general, O_A calculated as $1/2(H_T - H_A)$ was also equivalent, but this was not universal since a part of the oxygen adsorbed by some catalysts did not react with hydrogen. In general also, reproducible values of O_T and H_T were obtained in a sequence of titers $H_A \rightarrow O_T \rightarrow H_T \rightarrow O_T \rightarrow H_T$, but clearly this was subject to the same limitations.

Electron microscopy. The procedure used has already been described (*6*). Many of the catalysts studied contained extremely well-dispersed metal and had narrow size distributions. Excellent repeatability was obtained starting from different samples of the same batch in these cases. Catalysts with lower metal area contained a wider range of crystallite sizes and representative sampling was therefore more critical. Acceptable repeatability was obtained, but clearly the mean diameters could not be determined as accurately in such catalysts. Because of the statistical limitations introduced by a wide size distribution, catalysts were designed to avoid this problem as far as possible. For example, mean crystallite size can be varied by incremental increases in platinum loading, but extremely wide size ranges invariably result. Firing chemideposited platinum–silica catalysts in air produced the desired increase in crystallite size with a relatively narrow size distribution.

X-Ray diffraction: Debye line broadening was used as a measure of mean size when the platinum crystallites were sufficiently large. The peak width at half maximum of the (1,1,1) diffraction line was used, and the data were corrected for $k\alpha_1\alpha_2$ (filtered copper radiation) and instrumental line broadening. A value of 0.9 was assumed for the Scherrer constant.

Materials. Materials and catalyst preparation were described in Part I (*6*).

RESULTS

(a) **Platinum–Silica.** After "standard reduction" (see Experimental section), platinum–silicas prepared by impregnation with chloroplatinic acid contained platinum crystallites some 10–50 Å in size. These crystallites were well dispersed throughout the silica, and the size distribution obtained for a 2.8 wt % platinum sample yielded a surface mean diameter (*6*) of 31 Å. As shown in Table 1, hydrogen chemisorption on this sample gave an H/Pt value of about 0.4, and the ratios of $H_A:O_A:H_T$ were approximately 1.3:1:3.25. An 0.5 wt % platinum–silica prepared from chloroplatinic acid gave similar results after standard reduction.

Hydrogen adsorption and the hydrogen–oxygen titers were remeasured after overnight reduction at about 500°C. For both samples, H/Pt had declined significantly while O/Pt was about the same. In each case this led to $H_A:O_A:H_T$ ratios close to 1:1:3.

Small platinum crystallites were also detected on standard reduction of catalysts prepared by chemideposition (*8*, *9*). However, the platinum crystallites were smaller [surface mean diameter = 13 Å in a 2 wt % platinum–silica prepared by the method of Benesi, Curtis and Studer (*8*)], had a narrower size distribution (7–25 Å), and covered the silica more uniformly than in the case of the impregnated catalysts.

In keeping with these observations, a high H/Pt ratio was obtained after standard reduction of this sample (Table 1). $H_A:O_A:H_T$ was close to 2:1:4. An equivalent catalyst containing 0.5 wt % platinum gave broadly similar results, as did a 2.7 wt % platinum–silica prepared by the method of Poltorak and Boronin (*9*).

After prolonged treatment in hydrogen at 500°C, the adsorptive properties of all three samples changed in a similar way, which was also equivalent to the changes observed in the impregnated samples. H_A decreased, O_A remained almost constant, and consequently $H_A:O_A:H_T$ ratios close to 1:1:3 were obtained.

As shown in Table 1, measurements of CO_A on these silica-supported samples were always close to, but somewhat lower than, the corresponding hydrogen uptakes on a molecule/atom basis.

It may be inferred that each of these catalysts had similar stability to prolonged treatment in hydrogen once the initial platinum crystallites were formed, but that the different methods of contacting platinum ions and support had a marked effect on this initial size. The changes in size produced by the extended hydrogen treatment were small in either case. Indeed, a clear distinction was not possible from electron micrographs, since the extended treatment frequently seemed to create large crystals in localized areas rather than a universal increase in size.

However, as pointed out by Dorling and Moss (*10*), the distribution of crystallite size on platinum–silica may be varied by other means. They showed that if the oven-dried catalysts were heated in air prior to reduction, large platinum crystals were formed. In keeping with their findings, calcination, which is standard practice in the preparation of many catalysts, caused platinum sintering in all platinum–silica samples. In one series of experiments, several samples were oven-dried, placed in a crucible and calcined in air. The furnace was programmed at 2°/min, terminating in 2 hr at 500°C. Each contained large platinum crystallites some 30–120 Å in diameter, and it was found that similar effects were produced even if air was swept from the furnace and the heat treatment carried out in an inert atmosphere. When chemideposited catalysts containing about 2 wt % platinum were so treated in a nitrogen environment, H/Pt values in the range 0.2–0.3 were obtained after subsequent standard reduction. The microscope confirmed that these low hydrogen uptakes were related to real changes in crystallite size and showed that crystallites of the appropriate size were already present after the heat treatment alone. These were not changed significantly by the ensuing reduction in hydrogen.

TABLE 1
ADSORPTION AND SIZE DATA FOR SUPPORTED PLATINUM CATALYSTS

Catalyst	Initial treatment	Treatment in hydrogen	H_A (atoms $\times 10^{-19}$/g)	O_T (atoms $\times 10^{-19}$/g)	H_T (atoms $\times 10^{-19}$/g)	CO_A (molecules $\times 10^{-19}$/g)	O_A Calc. as $(O_T - 1/2H_A)$	$\frac{H}{Pt}$	$\frac{O}{Pt}$	$\frac{CO}{Pt}$	$\frac{CO}{H}$	H_A:O_A:H_T	Surface mean diameter from microscopy:	Mean diameter by X-ray diffr.
0.5% Pt/SiO$_2$[f]	*a*	Std. reduction	0.82	1.06	2.02		0.65	0.53	0.42			1.26:1:3.26		
	a	64 hr at 530°C	0.76	1.09	2.02		0.71	0.49	0.46			1.07:1:2.85		
2.8% Pt/SiO$_2$[f]	*a*	Std. reduction	3.10	3.94	7.76		2.39	0.36	0.28			1.30:1:3.25	31 Å	
	a	17 hr at 520°C	2.51	3.83	7.21		2.57	0.29	0.30			0.98:1:2.80		
2.0% Pt/SiO$_2$[g]	*a*	Std. reduction	7.08	7.93	16.47	5.88	4.39	1.15	0.71	0.95	0.83	1.61:1:3.75	13 Å	
	a	Std. reduction	8.37	8.96	19.08		4.77	1.35	0.77			1.75:1:4.00		
	a	17 hr at 520°C	6.07	8.26	16.19	5.56	5.23	0.98	0.85	0.90	0.91	1.16:1:3.09		
2.71% Pt/SiO$_2$[h]	*a*	Std. reduction	6.29	7.21	15.11		4.07	0.75	0.48			1.55:1:3.71		
	a	64 hr at 500°C	4.46	6.24	12.42	4.14	4.01	0.53	0.48	0.49	0.93	1.11:1:3.09	15 Å	
0.5% Pt/SiO$_2$[g]	*a*	Std. reduction	1.71	1.72	3.39		0.87	1.11	0.63			1.96:1:3.90		
2.0% Pt/SiO$_2$[g]	*a, b*	Std. reduction	1.81	1.82	3.22		0.91	0.29	0.15			1.99:1:3.55		
	a, b	17 hr at 520°C	1.24	1.70	2.72	0.70	1.08	0.20	0.17	0.11	0.56	1.15:1:2.52	91 Å	89 Å
3.6% Pt/Si$_2$[g]	*a, c*	Std. reduction	4.10	4.16	7.98		2.11	0.37	0.19			1.94:1:3.94		
	a, c	50 hr at 520°C	2.38	3.28	5.88		2.09	0.21	0.19			1.14:1:2.81		
	a, c, d	16 hr at 520°C	2.11	2.88	4.94	1.56	1.83	0.19	0.16	0.14	0.74	1.15:1:2.70	92 Å	81 Å
1.83% Pt/Al$_2$O$_3$[f]	*a, e*	Std. reduction	5.86	5.75	12.48		2.82	0.89	0.42			2.08:1:4.42		
	a, e	Std. reduction	6.01	6.06	12.24		3.06	0.76	0.54			1.96:1:4.00		
	a, e	17 hr at 520°C	4.44	5.92	11.69	3.51	3.70	0.67	0.56	0.53	0.79	1.20:1:3.16	12 Å	
0.7% Pt/Al$_2$O$_3$[f]	*a, e*	Std. reduction	1.22	1.45	3.13	0.91	0.84	0.53	0.36	0.39	0.75	1.45:1:3.73		
0.5% Pt/Al$_2$O$_3$[f]	*a, e*	Std. reduction	1.08	1.15	2.25	0.86	0.61	0.70	0.39	0.56	0.79	1.77:1:3.69		

[a] Oven dried at 120°C; [b] Heat treated in nitrogen environment at 500°C; [c] Fired in air at 500°C; [d] Fired in air at 550°C; [e] Calcined to 500°C; [f] Prepared by impregnation with chloroplatinic acid; [g] Prepared: by chemideposition per Benesi, Curtis and Studer (*8*); [h] Prepared by chemideposition per Poltorak and Boronin (*9*).

The adsorptive properties of two such samples were examined in detail. Both were prepared by chemideposition, which was found to yield narrower size distributions whatever the subsequent treatment. After oven drying, they were treated at about 500°C in oxygen and nitrogen, respectively; and after standard reduction, each gave H/Pt values of about 0.3. $H_A:O_A:H_T$ ratios were close to 2:1:4 despite the fact that some of the oxygen chemisorbed was not removed in the hydrogen titer (Table 1). (This was only observed on samples containing large platinum crystallites.) After treatment in hydrogen, these ratios approached 1:1:3 as before. Further treatment in oxygen at 500°C produced no further change at this time.

Crystallite sizes did not appear to change greatly as a result of the extra treatment in hydrogen, but crystallite shape did appear to change. The large crystals formed after short periods of high temperature treatment were irregular and poorly defined while prolonged reduction gave relatively sharp geometric forms, probably cubo-octahedra bounded by square (1,0,0) and hexagonal (1,1,1) faces. However, cubic habits could not be entirely ruled out.

The final size distributions of these two catalysts were little different, and there was reasonably good agreement between the mean size calculated from the micrographs and that obtained by Debye line broadening (Table 1). As shown in Table 1 also, CO_A was substantially lower than H_A on these two samples.

(b) Platinum–Alumina. A few platinum-alumina samples were examined for comparison. Air calcination of platinum–alumina is standard procedure in many laboratories, and unlike the platinum–silica samples, final platinum dispersion in these catalysts was unaffected by calcination at 500°C. Discrete platinum crystallites were not observed after oven drying or on subsequent calcination. They were detected after "standard" reduction. On a 1.8% platinum–alumina, these were extremely small (7–20 Å) and did not seem to be sufficiently numerous to account for the entire platinum loading. After 15 hr at 500°C, the mean size was little different, but considerably more platinum could be accounted for. This suggests that part of the platinum was present as units unresolved by the microscope after standard reduction.

As shown in Table 1, the adsorption data for three such catalysts, containing 1.8, 0.7 and 0.5 wt % platinum, were broadly similar to the results obtained for platinum–silica. After "standard" reduction, $H_A:O_A:H_T$ ratios were more nearly of the 2:1:4 type and approached 1:1:3 after prolonged treatment in hydrogen. However, as observed previously (*6*), the H_A values obtained initially for the 0.7 and 0.5 wt % platinum samples were lower than might be anticipated (*3*).

As with platinum–silica, each of these samples took up significantly fewer carbon monoxide molecules than hydrogen atoms (Table 1).

DISCUSSION

Hydrogen chemisorption. The relationship between platinum size and hydrogen uptakes at 25°C was examined in Part I of this series (*6*). The two were in acceptable agreement if it was assumed that each surface platinum atom adsorbed one hydrogen atom ($H/Pt_s = 1$). The present results confirm this trend and both are included in Fig. 1a, which compares H/Pt with the corresponding surface mean diameters (*6*) calculated from electron micrographs. The full line of Fig. 1a was calculated using the assumptions (*6*) of spherical geometry; 1.12×10^{15} surface platinum atoms/cm² and an H/Pt_s ratio of unity. The degree to which these assumptions are valid is examined more critically in Fig. 1b, in which the H/Pt ratios are compared to the appropriate Pt_s/Pt ratios calculated on the above model.

Several previous studies have included measurements of platinum size. Adams, Benesi, Curtis and Meisenheimer (*11*), for example, measured hydrogen chemisorption at 0°C on a platinum–silica catalyst and determined the mean crystallite size by both Debye line broadening and electron microscopy. Their calculation of Pt_s/Pt

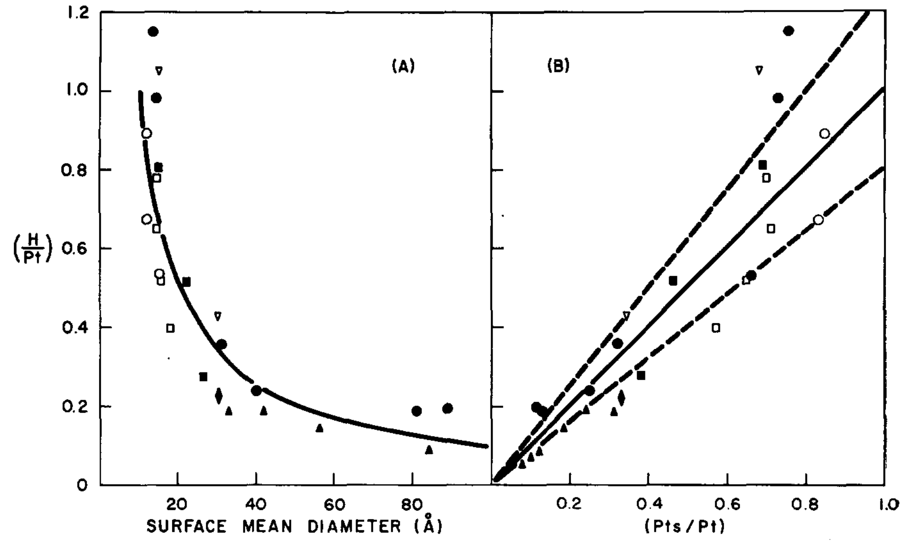

Fig. 1. Comparison of hydrogen chemisorption and platinum crystallite size, ○ present work; □ Wilson and Hall (*3*, *24*); △ Dorling, Burlace and Moss (*5*); ◇ Adams, Benesi, Curtis and Meisenheimer (*11*); and ▽ Zaidman *et al.* (*12*). Open points are for platinum–aluminas, closed points for platinum–silicas. In 1A, the line was calculated (*6*) assuming spherical geometry, $H/Pt_s = 1$ and 1.12×10^{15} platinum atoms/cm². In 1B, the full line represents a 1:1 correspondence of H/Pt and Pt_s/Pt, the dotted lines ±20% deviations from this 1:1 relationship.

was similar to that above, except that the area occupied by one platinum atom was taken as 11 Å². This corresponds to a surface site density of about 0.91×10^{15} platinum atoms/cm². Their data have been included in Fig. 1b, recalculated on the basis of 1.12×10^{15} platinum atoms/cm². Similarly, values of Pt_s/Pt were recalculated from the size distributions given by Wilson and Hall (*3*, *24*) who measured H_A by extrapolating 25°C isotherms to zero pressure. Zaidman *et al.* (*12*) used hydrogen uptakes at 250°C and 120 Torr to estimate H_A and reported detailed size distributions for two of their catalysts. They did not compare the two quantitatively, but their data have also been included in Fig. 1. Dorling, Burlace and Moss (*5*) measured H_A in the same way as Wilson and Hall but estimated Pt_s by a more complex method. They obtained a mean size >50 Å from Debye line broadening, estimated the weight of metal detected and hence included the contribution of crystallites <50 Å in diameter. The latter was taken to have a mean of 25 Å on the basis of electron micrographs. From this point, their calculations were similar to that employed here except that ⅙ of the platinum surface was assumed to be in contact with the support and therefore unavailable to hydrogen. Their data have been included in Fig. 1b by multiplying their overall Pt_s values by 1.2 and in Fig. 1a by back-calculating the appropriate mean diameters.

The full line of Fig. 1b represents a one-to-one correspondence between H/Pt and Pt_s/Pt and accordingly implies that H/Pt_s is equal to one. In contrast to the diverse opinions expressed in the literature, therefore, studies which include reliable measurements of platinum size support this one-to-one relationship ($0.1 < Pt_s/Pt < 0.9$) within acceptable limits. The X-ray diffraction data of Spenadel and Boudart (*13*), among others, extend this stoichiometry to larger crystals where similarity to bulk platinum might be anticipated.

Most of the points of Fig. 1b lie within the dotted lines which represent deviations of ±20%. This is probably in keeping with the uncertainties in independent measurements of size, and the calculation of Pt_s when mean size is known. Many points parallel the —20% deviation line, reflecting the excellent agreement obtained by Dorling, Burlace and Moss (*5*), who assumed that one face of a cubic crystallite was wetted by the support; and by Adams, Benesi, Curtis and Meisenheimer (*11*), who assumed a surface site density some 19% lower than employed here. However, all such calculations are necessarily simplistic, and the present model is preferred only because it provides better fit of all available data to a single set of assumptions. In fact, the surface atom density assumed has no geometric basis in either case. Cubo-octahedra are bounded by (1,1,1) and (1,0,0) faces, cubes entirely by (1,0,0). These have site densities of about 1.5 and 1.3×10^{15} atoms/cm^2, respectively, which suggests that either Pt_s is lower on the surface of the small, apparently cubo-octahedral crystallites than on extended planes of the relevent orientations, or alternatively, that an appreciable part of the crystallite surface is inaccessible to hydrogen. If on the other hand, this inconsistency is taken to indicate that H/Pt_s is not unity, then it favors a stoichiometry in which H/Pt_s is less than one.

Therefore, the data appear to exclude the possibility that $H/Pt_s = 2$ (*14*) and do not support the treatment given by Bond (*2*), which would predict, for example, that cubo-octahedral crystallites 30 Å in diameter yield H/Pt_s and H/Pt values of about 1.3 and 0.7, respectively.

The uncertainties associated with the measurements do not preclude less pronounced deviations. On the contrary, H/Pt values greater than one were observed on platinum–silica; and when H/Pt was about one, Pt_s/Pt appeared to be significantly less than unity. The latter could be due to the presence of crystallites not resolved by electron microscopy, but it seems more likely that H/Pt_s may exceed one on extremely small crystallites supported on silica. (Poltorak and Boronin (*9*) found H/Pt ratios as high as 1.3 on similar samples at 25°C.) In addition, Fig. 1 includes only one platinum–alumina of low metal content [an 0.16% platinum catalyst studied by Zaidman *et al.* (*12*)], mainly because it is difficult to size platinum in such samples. Therefore, the interpretation of hydrogen chemisorption on these samples remains uncertain (*3*, *12*, *15*, *16*).

With these possible exceptions, the available data show considerable accord despite the varied approaches. The estimation of platinum surface area by hydrogen chemisorption requires an experimental definition of monolayer coverage, and two such definitions have enjoyed widespread use, the zero pressure entrapolation of 25°C isotherms (*3*) and the adsorption at 250°C and about 200 Torr (*13*). Figure 1 suggests that when platinum is crystalline and observable by electron microscopy, an H/Pt_s ratio close to unity is obtained in either case and that the pulse adsorption results fit fairly well into this picture. This correlation encompasses the size range (15–70 Å) in which a large fraction of the surface platinum atoms have low coordination (*1*), in which unusual chemisorption behavior has been observed for other adsorbates (*1*, *3*) and in which large variations in H/Pt_s might be predicted (*2*).

Carbon monoxide chemisorption. Although chemisorption of carbon monoxide on supported platinum has been reported frequently, few studies contain sufficient data to determine adsorption stoichiometry. The only detailed comparison with measurements of size is that of Dorling and Moss (*4*) for the platinum–silica system. Their studies indicated that CO/Pt_s was about 0.87 on samples containing small platinum crystallites, but that this value decreases significantly on poorly dispersed catalysts ($Pt_s/Pt < 0.2$).

Comparison with other studies can be obtained by including investigations in which hydrogen and carbon monoxide adsorption were measured on the same catalysts. Thus the data of Dorling, Burlace and Moss (*5*), Gruber (*16*), Wilson and Hall (*3*) and the present work are compared in Fig. 2. CO/H is plotted against H/Pt, where CO/H is the ratio between the numbers of carbon monoxide molecules and hydrogen atoms taken up by each sample. The work of Dorling and Moss (*4*) has also been included. They compared CO_A with Pt_s/Pt, and their data have been

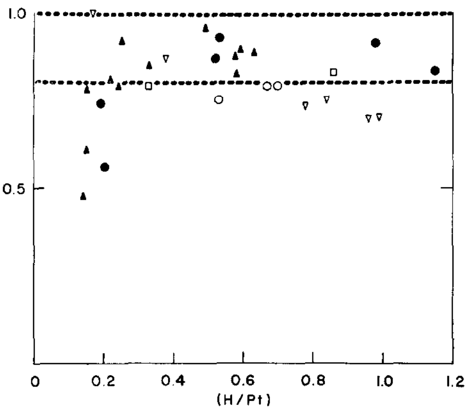

FIG. 2. Comparison of hydrogen and carbon monoxide chemisorption on supported platinum, CO/H being on a molecule/atom basis. ○ present work; △ Moss, *et al.* (*4, 5*); □ Wilson and Hall (*3*); ▽ Gruber (*16*). Open points are for platinum–aluminas, closed points for platinum–silicas. The dotted lines are at CO/H ratios of 1.0 and 0.8.

used in Fig. 2 on the assumption that $H/Pt_s = 1$.

Clearly the present results follow the relationships established by Dorling and Moss (*4*) for platinum–silica catalysts. For H/Pt greater than about 0.25, all points lie within the range $0.83 \leq CO/H \leq 0.96$. Below $H/Pt = 0.25$, CO/H and therefore CO/Pt_s decrease dramatically. Steric factors provide a possible explanation of this behavior. The electron microscope suggests that the crystallites observed on silica below $H/Pt = 0.25$ are cubo-octahedra bounded by (1,0,0) and (1,1,1) faces; and calculation suggests (*17*) that, while a CO/Pt_s ratio close to one may obtain on a (1,0,0) plane, the limiting ratio on a (1,1,1) plane is about 0.33.

There is an alternative explanation. Eischens and Pliskin (*18*) observed two infrared absorption bands for carbon monoxide on supported platinum and ascribed these lower and higher energy bands to linear and bridge-bonded species, respectively. They found that the latter accounted for some 15% of the total adsorbed carbon monoxide on a platinum–silica catalyst, but about 50% of the total uptake on platinum–alumina. Many rationalization of carbon monoxide chemisorption on platinum are based on this classic study, since it permits an assignment of $CO/Pt_s = 1$ for the linear form and $CO/Pt_s = 0.5$ for the bridged species. Insofar as adsorption data can be treated in this way, the results for platinum–silica in Fig. 2 imply that the higher energy ir band should predominate on larger crystals ($H/Pt < 0.25$), causing the low CO/Pt_s ratio. Infrared studies of carbon monoxide adsorption on supported nickel (*19*) and palladium (*20*) suggest that this may indeed be the case. However, the recent data reported by Van Hardeveld and Hartog (*21*) support an alternative model (*22*), which ascribes the higher energy band to linearly sorbed carbon monoxide on surface atoms of low coordination. This model predicts the appearance of the high energy band 15 Å < *d*-sphere < 70 Å and does not allow an assignment of $CO/Pt_s = 0.5$ because of bridge-bonding. For the present, therefore, the decrease in CO/Pt_s on large platinum crystals is probably best ascribed to the spatial restrictions which govern carbon monoxide chemisorption on a (1,1,1) face.

By inference, there can be little steric hindrance of carbon monoxide chemisorption on platinum–silica above $H/Pt = 0.25$. It follows that the surface platinum atoms must be less densely packed than on a (1,1,1) face, which is in keeping with the low surface atom density which gave best fit to the hydrogen adsorption data. Nevertheless, carbon monoxide uptakes were always less than the corresponding amounts of hydrogen. This is consistent with an H/Pt_s ratio of one, CO/Pt_s being somewhat lower (*4*); but the independent methods of estimating Pt_s are probably not sufficiently accurate to distinguish which of H_A or CO_A best measures Pt_s on small platinum crystallites.

Gruber's data for platinum–alumina are clearly dissimilar to the trends observed on platinum–silica. His results showed minimum CO/H ratios when the platinum was best dispersed, CO/H being about 0.7 when H/Pt was approximately one. Gruber suggested that this was due to 50% bridge-bonding on the well-dispersed samples, again based largely on the work of Eischens and Pliskin. However, Gruber measured hydrogen chemisorption by the conventional method and carbon monoxide chemisorption by a pulse method. Since the latter excludes weak chemisorption, an alternative explanation of the results is possible. However, further work is required in this area, particularly with respect to the existence or non-existence of bridged carbon monoxide species, since it seems less than satisfactory to rationalize discrepancies between hydrogen and carbon monoxide uptakes in terms of bridge-bonding without the relevant infrared spectra.

Oxygen adsorption and hydrogen–oxygen titration. Benson and Boudart (*23*) introduced the titration of presorbed oxygen with hydrogen as a measurement of platinum dispersion. They assumed that supported platinum would behave as platinum black, so that $H_A:O_A:H_T$ would be 1:1:3. A single determination of O_A did yield an H_T/O_A ratio of about 3.2. Mears and Hansford (*14*) later found 2:1:4 ratios on a variety of supported platinum catalysts, and subsequently, Wilson and Hall (*3*) showed that either ratio or intermediate values could obtain. Wilson and Hall concluded that these changing ratios were due to changes in the stoichiometry of oxygen chemisorption on platinum. They suggested that approximately one oxygen atom was adsorbed per two surface platinum atoms on small crystallites, while a one-to-one relationship was approached on large crystallites.

Comparisons of hydrogen and oxygen chemisorption are collected in Fig. 3, which includes the work of Mears and Hansford (*14*), Wilson and Hall (*3, 24*) and Buyanova, Ibragimova and Karnaukhov (*15*). The data for platinum–aluminas containing less than 0.2 wt% metal have been omitted. These gave H/Pt and O/Pt values substantially greater than one (*15*) and may have unique properties. Studies in which O_A was measured at elevated temperature have also been omitted, since Gruber (*16*) showed that oxygen penetrates the platinum surface at high temperatures.

In Fig. 3a, O/Pt is plotted vs H/Pt and the data are differentiated with respect to author and support. The solid lines of Fig. 3a represent the limiting cases $O_A/H_A = 0.5$ and $O_A/H_A = 1.0$, which must, in turn, give $H_A:O_A:H_T$ ratios of 2:1:4 and 1:1:3 if the titers are reversible. Clearly, there-

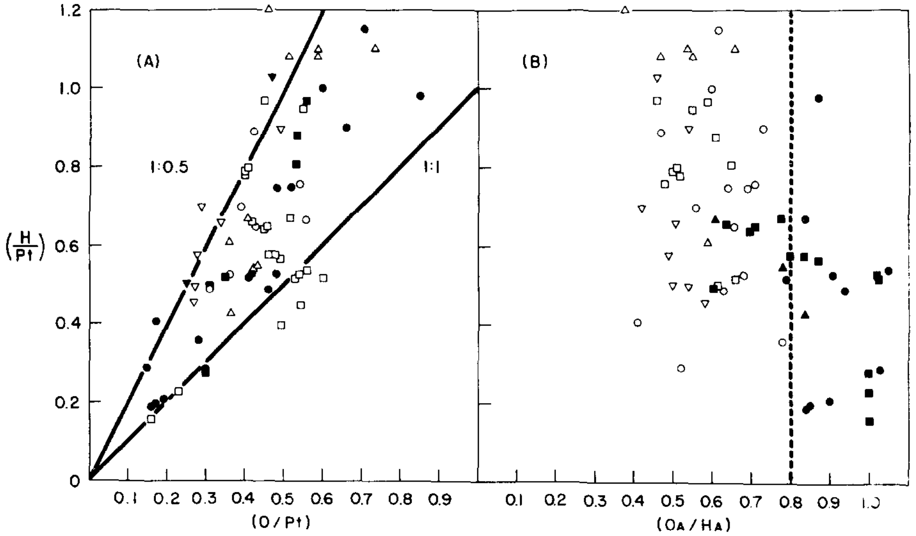

FIG. 3. Comparison of hydrogen and oxygen chemisorption on supported platinum catalysts. ○ present work; □ Wilson and Hall (*3, 24*); △ Buyanova, Ibragimova and Karnaukhov (*15*); ▽ Mears and Hansford (*14*). In 3A, the open points are for platinum–aluminas, the closed points for platinum–silicas. In 3B, there is no distinction of supports, the open points are for samples given "mild" reduction and the closed points for samples given "prolonged" reduction (see text). The lines of 3A are for O_A/H_A ratios of 0.5 and 1.0.

fore, all available measurements confirm that either ratio may be obtained and that intermediate values are common. However, no reasonable correlation of the ratio O_A/H_A with H/Pt, and thus dispersion, is apparent.

Since the duration of high temperature treatment in hydrogen seemed to be important (Table 1), we have attempted to differentiate the available data on this basis. Samples given a "mild" reduction have been distinguished from those given "prolonged" treatment in hydrogen. The distinction is necessarily rather crude; but "mild" reduction has been arbitrarily defined as 1–3 hr at 500°C, "prolonged" reduction as exceeding 15 hr at 500°C, or the equivalent at higher temperatures as best this may be judged. In Fig. 3b, O_A/H_A is compared to H/Pt on this basis.

As pointed out by Wilson and Hall (*3*), changes in the ratio O_A/H_A question whether H/Pt or O/Pt is more properly a function of platinum dispersion. The present study tends to support their suggestion that H/Pt provides the better correlation with crystallite size. Fig. 1b suggests that H/Pt_s is approximately equal to unity, while Fig. 3b shows that O_A/H_A varies between 0.4 and 1.0. However, it is clear again that the value of O_A/H_A is not primarily a function of H/Pt. Rather, all samples given "mild" reduction yield values in the range $0.4 \leq O_A/H_A \leq 0.8$. (Indeed, with the exception of the present work, which will be biased if there is appreciable reversible adsorption of hydrogen (*6*), none exceed 0.7.) Samples given "prolonged" treatment in hydrogen on the other hand are predominantly in the range $0.8 < O_A/H_A < 1.0$. However, the distinction is not clear-cut. Several points, which were obtained for platinum–alumina samples containing less than 1 wt % platinum (*3, 15*) still show relatively low O_A/H_A values after "prolonged" reduction. Therefore, thermal history does not uniquely determine O_A/H_A, and yet another anomaly occurs with platinum–aluminas at low metal loading.

In keeping with the findings of Wilson and Hall, the present results show that O_A remains reasonably constant or increases very slightly, as the duration of reduction is increased (Table 1). Therefore, changes in O_A/H_A are due primarily to decreases in H_A. It follows that O_A is probably smaller than Pt_s after "mild" treatment and about equal to Pt_s when the treatment is "prolonged". Presumably, these changes reflect the surface structure of the platinum crystallites. It seems reasonable to suppose that after "mild" reduction the metal crystallites formed may still have high surface energy. Each has been formed from some chance number of metal atoms and probably contains many ad-atoms and other surface atoms of low coordination. "Prolonged" treatment at 500°C must be expected to cause the equilibration of these defective structures. Minimum energy forms with the least possible surface unsaturation would be expected. It would be surprising if such changes did not cause subtle differences in hydrogen adsorption capacity for a crystallite of any given size, but changes in the interaction with oxygen seem to be more pronounced. The modification of large platinum crystallites produced by prolonged treatment in hydrogen and observed in the electron microscope is consistent with such structural equilibration.

CONCLUSIONS

The chemisorption of hydrogen on a single sample of platinum is highly complex. It is scarcely surprising therefore that the measurement of surface area in this way has been subject to controversy. Nevertheless, all studies which contain detailed measurements of crystallite size indicate that, within reasonable limits, each surface platinum atom adsorbs one hydrogen atom. Indeed, the agreement is remarkably good when it is considered that the data were obtained in different laboratories, frequently using different criteria to define the hydrogen monolayer.

It follows that hydrogen chemisorption on small platinum crystallites is not very different to that on bulk platinum, that adsorption on the metal is successfully distinguished from that on the support and that there is no apparent distinction between alumina- and silica-supported platinum on this basis. However, uncertainties in the independent measurement of Pt_s may mask subtle differences. Indeed, there is evidence that H/Pt_s may exceed one on platinum–silica when the crystallites are extremely small, and that the correlation may not include platinum–aluminas at low metal loading. When freshly reduced, the latter contain platinum at least partly unresolved in the microscope and show unusual adsorptive properties.

The stoichiometry of carbon monoxide chemisorption is also reasonably constant on small platinum crystallites and could conceivably correspond to CO/Pt_s equal to one with H/Pt_s some 15–20% higher. The independent measurements of size are not precise enough to distinguish between this and the preferred explanation in which H/Pt_s is equal to one. Large platinum crystals adsorb much less carbon monoxide than hydrogen, which appears to be due to a decrease in CO/Pt_s, and may be caused by steric hindrance on extended planes of (1,1,1) orientation. There may be differences between carbon monoxide chemisorption on platinum–alumina and platinum–silica, but the available data are open to various interpretations.

The volume of oxygen taken up by supported platinum catalysts does not bear a constant relationship to the corresponding volume of hydrogen. This is ascribed largely to changes in the stoichiometry of oxygen chemisorption on the platinum surface, and seems to be related to the thermal history of the sample. After long high-temperature treatment in hydrogen, the surface behaves like that of platinum black, adsorbing almost equal quantities of hydrogen and oxygen. Shorter treatments yield hydrogen uptakes much greater than those of oxygen.

Hydrogen chemisorption must therefore be recommended as the best determinant of platinum surface area. The stoichiometry of hydrogen chemisorption appears to be relatively constant over a wider range of crystallite size. Uncertainties in the stoichiometry of carbon monoxide adsorption on large crystals, and of the stoichiometry of oxygen adsorption over essentially the entire range of interest, make them less desirable for this use. It follows that the interpretation of hydrogen–oxygen titers will be difficult at best.

The available hydrogen chemisorption data suggest that interatomic distances in the surface of small platinum crystallites may be appreciably higher than for perfect cubes or cubo-octahedra. The high CO/Pt_s ratios observed above $H/Pt = 0.25$ are consistent with this picture, since steric factors may not permit high CO/Pt_s ratios on the more densely populated faces of platinum.

Thermal history may be important, not only as a determinant of crystallite size, but also as it pertains to the equilibration of crystallite structure and the corresponding degree of surface unsaturation.

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