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A Comparison of Gas-Phase and Electrochemical Measurements for Chemisorbed Carbon Monoxide and Hydrogen on Platinum Crystallites

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Hydrogen and carbon monoxide chemisorptions have been measured by gas-phase and electrochemical methods for platinum dispersed on carbon supports. At both the liquid and gas-phase interfaces, the stoichiometries of the chemisorptions were similar; the ratio of hydrogen atoms to surface platinum atoms was close to unity, and the ratio of CO molecules to hydrogen atoms adsorbed lay between 0.8 and 1.0 for platinum crystallites up to 200 Å in diameter. In gas-phase measurements, catalyst pretreatment conditions must be carefully controlled to avoid poisoning of the platinum surface. The effectiveness of high anodic potentials in cleaning poisons from the platinum surface makes the electrochemical measurement an attractive complementary technique for the study of platinum supported on carbon.

INTRODUCTION

The recent papers of Freel (*1*), and Hall and Wilson (*2*) have reviewed current knowledge of the stoichiometry of hydrogen and carbon monoxide gas-phase chemisorption, on platinum crystallites supported on silica and alumina. They concurred that at room temperature, over a wide range of platinum crystallite diameters, chemisorbed hydrogen saturation coverage corresponds to about one hydrogen adsorbed per surface platinum atom. By making the assumption of spherical geometry for the crystallite and a surface platinum atom density of 1.12×10^{15} atoms/cm^2, reasonable agreement was obtained between the crystallite size calculated from hydrogen chemisorption data and that observed by electron microscopy ($\pm 20\%$). On the other hand, the number of CO molecules was less than the available surface platinum atoms assuming only linear CO chemisorption resulting in a CO molecule/H atom ratio (CO/H) of between 0.83 and 0.96 for platinum crystallites less than about 60 Å in diameter. For larger crystallites this ratio decreased.

Chemisorption of hydrogen and carbon monoxide on platinum has been of interest in electrochemical systems, apart from the intrinsic chemical interest, for a determination of the crystallite sizes of dispersed platinum on conductive supports. The electrochemical measurements of adsorbed hydrogen on platinum sheet electrodes in acid media were compared to gas-phase Krypton adsorption measurements and a charge of 210 μcoul/cm^2 was associated with the adsorbed hydrogen (*3*) monolayer. This value corresponds to 1.26×10^{15} atoms/cm^2 and has been used for both platinum sheet (*4*) and highly dispersed platinum (*5*). As with the gas-phase measurements, there is considerable variation in the numerical value used, which may be as low as 190 μcoul/cm^2 (*6*, *7*).

Since the value assigned to the number of surface sites, or surface platinum atoms, is dependent on the relative distributions of platinum crystal faces exposed, this will be a particular property of the individual platinum catalyst. Furthermore, for the same catalyst sample, the value assigned will apply equally to gas-phase or electrochemical measurements unless there are different steric requirements for the accommodation of hydrogen on platinum in the liquid and the gas phase.

The stoichiometry for the chemisorption of CO on platinum electrodes is less well established. Blurton *et al.* (*7*) found the ratio of charges associated with CO and H chemisorption to be 2.0 ± 0.1 for platinum black and platinum on graphite, corresponding to a CO molecule/H atom ratio of 1.0 ± 0.05. (The oxidation of a linearly adsorbed CO molecule on a single platinum-atom site would require two electrons, whereas an adsorbed hydrogen atom on the same site requires only one electron.) On highly dispersed platinum on carbon they found the CO/H ratio to be 0.75–1.0. Recently, Stonehart (*8*) measured the saturation coverage of CO on platinum wires and obtained a CO/H ratio of 0.9 ± 0.05 whereas Brummer and Ford (*9*) reported a value of 0.88 ± 0.09.

The constraint for electrochemical measurements is that the platinum catalyst support be electrically conductive, virtually restricting the choice of support for high surface area platinum to carbon. This paper describes a comparison of gas-phase and electrochemical measurements for carbon monoxide and hydrogen chemisorbed on the same platinum-on-carbon catalysts. It shows that despite the very different environment at the interface, similar stoichiometry obtains.

Experimental Details

Catalysts

Platinum was supported on two carbon blacks (Spheron 6 and Vulcan XC-72, Cabot Corp.), both of which had been graphitized at 2700°C. Solutions of platinum diammino dinitrite in nitric acid were added to the carbons in sufficient proportions to give the desired platinum to carbon ratios. The slurries were then reduced to dryness on a hot plate. The platinum oxide and nitrate so formed were decomposed by heating in air at 500°C for two hours. Subsequent pretreatment of the catalysts for gas-phase chemisorption, or electrochemical measurement, is described below.

Gases

Both hydrogen (Matheson CP Grade) and carbon monoxide (Linde CP Grade) used for gas-phase chemisorption measurements were purified by passage through 0.5% Pd on asbestos catalyst at 350°C, followed by a trap containing zeolite at −194°C.

Gas-Phase Chemisorption

A conventional glass BET volumetric apparatus was used.

The catalyst pretreatment temperatures were selected to give reduction of surface platinum oxide and desorption of hydrogen from the platinum surface while being held low enough to minimize the sintering of the platinum on the carbon supports.

The pretreatment used in most experiments was reduction with hydrogen at 300°C for three hours followed by evacuation at 10^{-5} mm Hg at 350°C for three hours. The chemisorption measurement was made at 24°C ± 1°C and at gas pressures between 30 and 400 mm Hg. Upon exposure to H_2 or CO a rapid adsorption occurred which was complete in 10 min. There was some reversible adsorption of CO and hydrogen associated with the carbon support. This was corrected by extrapolation to zero pressure, the correction being the largest for the catalysts with the lowest ratios of platinum to carbon (Fig. 1).

When the reduction step was incomplete, subsequent chemisorption of CO or hydrogen at room temperature showed a slow adsorption of both hydrogen and CO, following the rapid initial chemisorption. More complete reduction of the catalyst reduced this effect, though it was never entirely eliminated; so that a slow adsorption was present which could represent as much as 30% of the total in 24 hr. This appeared to be associated with carbon surface oxides as it was more pronounced on carbons which had been heavily oxidized by chemical means prior to catalyzing

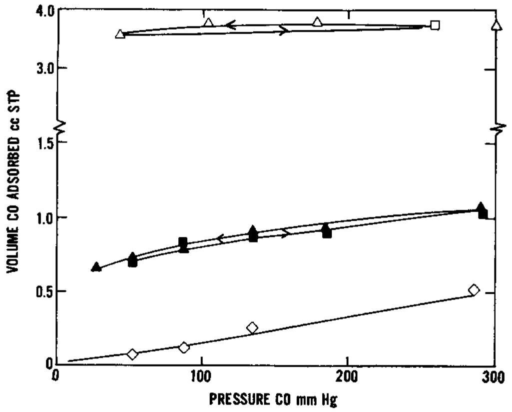

FIG. 1. Adsorption of CO on catalysts as a function of pressure. △ 20% Pt graph. Spheron 6; □ 0.527 g catalyst; ▲ 1% graph. Vulcan XC-72; ■ 2.11 g catalyst; ◇ 2.1 g graph. Vulcan XC-72.

with platinum. An example of this behavior is shown in Fig. 2. The rapid initial adsorption was taken to be the chemisorption of the gas on platinum.

The pretreatment temperature of 350°C was shown to be sufficient to desorb CO from the platinum surface, in the series of experiments reported in Fig. 3. After adsorption of CO on a well-sintered platinum catalyst, evacuation at successively higher temperatures raised the subsequent CO adsorption until a constant value was reached at about 350°C.

Electrochemical Measurement of Hydrogen and Carbon Monoxide Chemisorption

Electrochemical measurements were made in a three compartment cell in which the working electrode was separated from a gold counter electrode by a glass frit and the standard hydrogen reference electrode accessed to the working electrode by a Luggin capillary. The electrolyte was 20% H_2SO_4 (Fisher) maintained at 24 ± 1°C.

A potentiostat and function-generator enabled potentiodynamic sweeps to be made on the working electrode. The theory of the potentiodynamic technique, where the electrode potential is perturbed as a linear function of time while the current generated by the surface processes is recorded, has been published elsewhere (*10–12*).

The catalyst to be studied was fabricated into an electrode in the following manner: A porous film of PTFE tape was pressed onto a 325 mesh gold screen. A known weight of the catalyst (~10 mg) was ultrasonically dispersed in isopropanol together with 5 wt % TFE 42. This suspension was then filtered onto the PTFE tape, the filtered layer pressed and the whole electrode sintered for 5 min at 325°C. This electrode was then mounted in the working electrode compartment with a gold wire clip. The TFE 42 is necessary to maintain the structural integrity of the catalyst layer. The preparation and behavior of similar porous electrodes has been described by Vogel and Lundquist (*13*).

To insure that the catalyst layer was completely wetted by the electrolyte prior to the electrochemical measurement, the electrode was soaked in concentrated nitric acid, washed, placed in the working electrode compartment and potentiodynamically cyled once between hydrogen evolution, which reduced platinum oxide, and

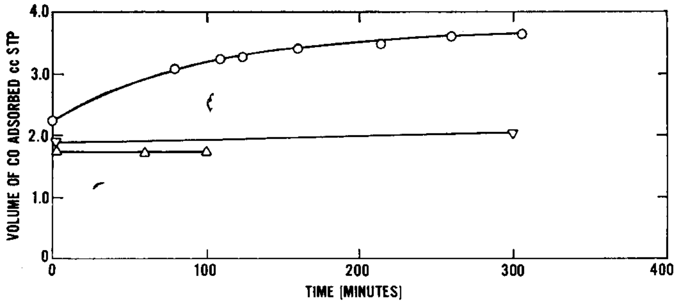

FIG. 2. Adsorption of CO as a function of time on 20% Pt on Graphon after various pretreatment conditions. ○ 250°C, H_2, 3 hr, ▽ 350°C, 4 hr, △ 370°C, 3 hr: 0.52 g catalyst.

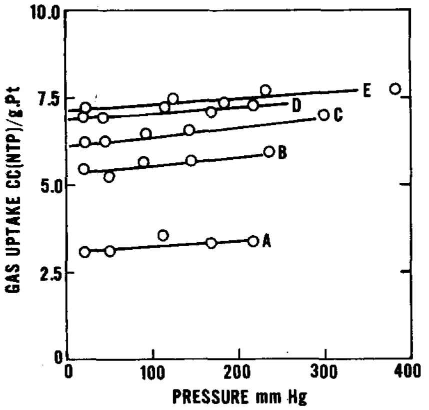

FIG. 3. Adsorption of CO on 20% Pt on carbon after evacuation at several temperatures. A 250°C, 3 hr; B 330°C, 3 hr; C 350°C, 3 hr; D 385°C, 3 hr; E 435°C, 3 hr.

1200 mV vs H_2 which oxidized any surface poisons. Electrolyte was drawn into the pore structure as the evolved hydrogen gas was oxidized. The electrode was then held at 700 mV for 1 min to reduce platinum surface oxide and swept cathodically at 8 mV/sec, during which the charge due to hydrogen adsorption on the platinum was recorded.

A typical potentiodynamic sweep curve for platinum black is shown in Fig. 4. Platinum supported on carbon gave similar curves. The various features of the curve have been described in the literature describing the potentiodynamic technique (*10–12*). The solid line which is the curve obtained in the absence of CO, shows the normally observed peaks associated with hydrogen deposition and oxidation and with oxide formation and reduction. Hydrogen coverages were calculated from the measured charge due to cathodic hydrogen deposition including both the strongly and weakly adsorbed hydrogen peaks (*10*). The base line was taken as the extrapolation of the double layer charging current from 400 mV to 50 mV.

To measure CO chemisorption, the electrode was subjected to the same potential pretreatment cycle as for hydrogen adsorption and then held at 50 mV vs H_2 while being flushed with CO gas. The electrolyte was then flushed with N_2 for 10 min to remove dissolved CO. The potential was swept anodically at 40 mV/sec, while the charge due to the oxidation of adsorbed CO, which appeared as a current peak at 830 mV (dotted line, Fig. 4) was measured. Experiments with longer periods of flushing with CO confirmed that saturation coverage had been reached, while longer periods of flushing with N_2 indicated the desorption was negligible at 50 mV. It should be noted that saturation of the surface with CO resulted in the complete elimination of adsorbed hydrogen from the surface.

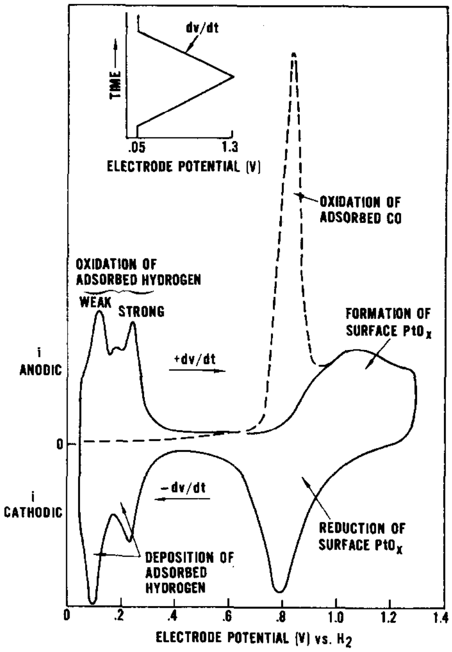

FIG. 4. Potentiodynamic sweep of platinum. Solid line 20% H_2SO_4, N_2. Dashed line 20% H_2SO_4, CO, 30 min, N_2 10 min, 24°C.

The quantities of hydrogen atoms and carbon monoxide molecules adsorbed were calculated from the associated charges, assumed 1 and 2 electron transfers, respectively.

RESULTS

Using the procedures described above, the gas-phase chemisorptions of CO and H_2 were measured after successive pretreatment cycles for 20% Pt on graphitized Spheron 6. The volume of gas adsorbed

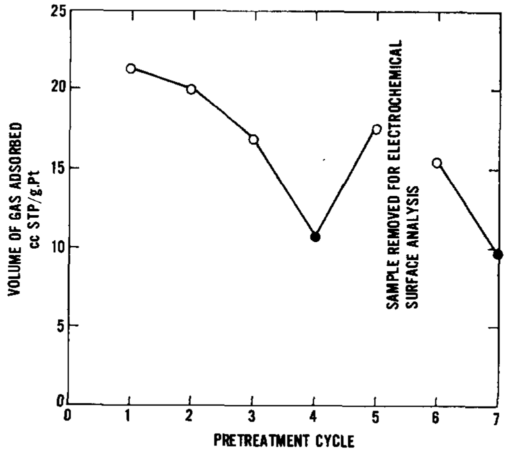

FIG. 5. Chemisorption of CO and H_2 on 20% on Graphon. ○ CO; ● H_2.

decreased with each cycle, due to sintering of the platinum, until a steady value was reached between the third and fifth cycle (Fig. 5). At this point, the adsorption of hydrogen and carbon monoxide could be compared with bracketed values. After the fifth pretreatment cycle a sample of the catalysts was removed for the determination of the electrochemical adsorption of carbon monoxide and hydrogen, following which the gas-phase chemisorption measurement was repeated. The data from these experiments, which present a comparison between the gas-phase and electrochemical measurements, are shown in Table 1 where the order from left to right is chronological.

It is apparent that the quantity of chemisorbed hydrogen and carbon monoxide measured electrochemically is higher than the corresponding value measured by gas-phase chemisorption on the same sample, while the CO molecule/H atom ratio, in both instances is less than unity.

In a second series of experiments, gas-phase chemisorption was measured on a series of catalysts comprising 1, 5 and 20% Pt on graphitized Vulcan XC-72. Observed adsorption after successive pretreatment cycles is plotted in Fig. 6. Here the adsorption measured on the 1% catalyst did not decline, suggesting a resistance to sintering at this low loading, whereas on adsorption the 5% Pt catalyst showed a steady decrease. Adsorption on the 20% Pt, however, showed little decrease but here the platinum appeared to have been severely sintered by the initial pretreatment, since adsorption measured electrochemically on the fresh catalyst was very much higher (Table 2). In this respect this catalyst differs from that of Fig. 1, where graphitized Spheron 6 was the support.

In Table 2, the initial hydrogen adsorption of Fig. 5 is compared to the electrochemical hydrogen adsorption measured on the fresh catalyst. Again the electro-

TABLE 1

COMPARISON OF CHEMISORPTION OF CARBON MONOXIDE AND HYDROGEN MEASURED ELECTROCHEMICALLY AND FROM THE GAS-PHASE

	Molecules or atoms adsorbed per g platinum × 10^{-20}								
	Gas-phase			Electrochemical			Gas-phase		
Sample[a]	CO	H	CO/H	CO	H	CO/H	CO	H	CO/H
20% Pt on graphitized Spheron 6 H_2 250°C, 2 hr Vac. 350°C, 2 hr	4.8	5.9	0.82	6.1	6.6	0.93	4.4	5.0	0.88
20% Pt on graphitized Spheron 6 H_2 250°C, 2 hr Vac. 500°C, 1 hr	3.8	4.7	0.81	—	6.7	—	4.2	6.6	0.64

[a] Data taken as described in text, with chronological order from left to right.

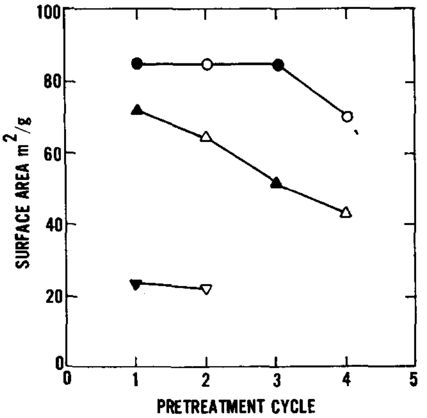

FIG. 6. Surface area of various Pt on graphitized Vulcan XC-72 catalysts by gas-phase chemisorption. Calculated assuming: 1.12×10^{15} H Atoms/cm² Pt (open points); 0.95×10^{15} CO Molecules/cm² Pt (closed points). ○ 1% Pt; △ 5% Pt; ▽ 20% Pt.

chemical measurement gave the higher value. No electrochemical measurement was possible for the 1% platinum catalyst because of interference from the double layer capacitance of the carbon. The CO/H ratio for the 5% Pt catalyst is taken from bracketed values in Fig. 6.

In another series of gas-phase experiments, the quantity of chemisorbed hydrogen was measured at room temperature, after which the temperature was raised in several steps to 400°C and the extent of gas-phase chemisorption measured at each step. The volume of hydrogen adsorbed was independent of pressure at each temperature but the saturation coverage decreased with temperature. At 400°C the volume of hydrogen increased slowly with time although at room temperature the adsorption had been constant for 15 hr.

Finally, in Table 3 the results are shown for BET nitrogen adsorption measurements on two platinum blacks of different surface area. The surface areas obtained from these measurements were in reasonable agreement with surface areas calculated from electrochemical hydrogen adsorption. A platinum black physically mixed with carbon gave a similar result. In the same table are listed CO molecule/H atom ratios determined electrochemically.

It was hoped that a comparison could be made between a physical measurement of Pt particle size and data obtained by adsorption measurements on supported platinum. X-ray line broadening techniques proved insufficiently accurate for the well dispersed samples, and direct transmission electron micrography was not possible in carbon. The recently developed dark field electron microscopy technique (*14*), however, was applied to a 20% Pt on graphitized Vulcan XC-72 which had given an electrochemically determined surface area of 70 m²/g. The particle size distribution measured by the dark field technique gave a surface area of 60 m²/g calculated from the surface area averaged particle diameter.

DISCUSSION

A most important consideration in any study of platinum supported on carbon must be the pretreatment condition used

TABLE 2

CHEMISORPTION OF CARBON MONOXIDE AND HYDROGEN ON VARIOUS PLATINUM ON CARBON CATALYSTS[a]

Sample	Molecules or atoms adsorbed per g Pt $\times 10^{-20}$				
Wt % Platinum on graphitized Vulcan XC-72	H Electrochemical	H Gas-phase	CO Gas-phase	CO/H Gas-phase	Surface area m²/g Gas-phase
1	—	9.7	8.2	0.85	85
5	10.8	8.3	6.6	0.80	74
20	6.1	2.8	2.2	0.81	25

[a] Calculated from H adsorption assuming 1.12×10^{15} atoms/cm².

TABLE 3

SURFACE AREA OF PLATINUM CATALYSTS MEASURED ELECTROCHEMICALLY AND BY BET NITROGEN ADSORPTION

	BET surface area m²/g	Electrochemical area m²/g Pt[a]	Electrochemically determined CO/H
Pt black	24.5	22.5	0.87
Pt black (sintered)	12.7	12.8	0.89
10% Pt black[b] on graphitized Spheron 6	24.5	30.0	0.89
20% Pt on graphitized Spheron 6	—	60.0	0.90

[a] Physically mixed.

[b] Calculated from Q_H assuming 0.180 mCi/cm².

to prepare the platinum surface. As Boudart (*15*, *16*) has pointed out, the high temperatures normally used to pretreat platinum on oxide supports are sufficient, in the case of carbon, to decompose surface oxides to form CO. The CO may then disproportionate to give carbon impurities on the platinum surface. Gas-phase oxidation of these impurities will lead to the formation of further carbon oxides. Because of these possibilities it was necessary to select a pretreatment temperature lying just below the temperature at which CO is desorbed from the carbon surface. Rivin (*17*) has shown this point to be about 400°C; below this temperature CO_2 and H_2O are the major products desorbed. The results shown in Fig. 3 suggest that 350°C is sufficient to desorb CO from the platinum surface with a minimum of disproportionation. Since the measured CO chemisorption did not decrease as the temperature was raised to 480°C disproportionation of the chemisorbed CO could not have been a serious source of carbon poisons. It should be noted that the graphitized carbons used in this work have a much lower carbon oxide content than the ungraphitized Spheron 6 used by Boudart (*15*, *16*) and would, therefore, generate a much smaller quantity of CO and CO_2.

In measuring the adsorption of hydrogen at 300–400°C on platinum supported on carbon, Boudart noted a "spillover" effect. Hydrogen in excess of that adsorbed on the platinum, was taken up by migration to the carbon surface. This effect is much reduced at room temperature and in the work reported here, was only observed when the temperature was raised to 400°C, or when the catalyst was incompletely reduced in the pretreatment. The slow uptake of CO shown in Fig. 2 appeared to be associated with the incomplete reduction of the catalyst and could be reduced to a rate which clearly differentiated it from the rapid chemisorption on the platinum surface.

A low pretreatment temperature was also desirable to minimize the sintering of the supported platinum noted here and in the work of Hillenbrand and Lacksonen (*18*). The catalyst of Fig. 5 and the 5% platinum catalyst of Fig. 6 showed surface area loss due mainly to sintering, since the 1% catalyst showed much less of this effect. The 20% platinum catalyst of Figs. 3–6 was already severly sintered by the initial pretreatment since the electrochemical surface area measurement on the same catalyst showed very much higher initial hydrogen adsorption.

Because of this sintering effect it was necessary to compare the electrochemical and gas-phase measurements on a catalyst which had already reached a more stable platinum crystallite size distribution. The experiments of Fig. 5 and Table 1 make this comparison. It is evident that the hydrogen adsorption obtained from gas-phase chemisorption varies from 70% to close to 100% of the electrochemically measured hydrogen adsorption. The variation in the gas-phase values reflect the difficulty in cleaning the platinum surface by gas-phase techniques. The electrochemical potentiodynamic pretreatment cycle to 1200 mV vs H_2 is sufficient to oxidize effectively hydrocarbon impurities on the platinum surface. Within the experimental error, the stoichiometries of the electrochemical and gas-phase adsorption for hydrogen on platinum were the same.

Calculated electrochemical surface areas using 1.12×10^{-15} H atoms per cm^2 were in good agreement with the BET measurement of the two platinum blacks in Table 3. Furthermore, the dark-field electron microscopy measurements of supported platinum were in reasonable agreement with the electrochemical measurements. Within the terms of the discussion of Freel, and Hall and Wilson for platinum on oxide supports it appears, therefore, that the ratio of hydrogen to surface platinum atoms, H/Pt_s, for platinum supported on carbon, was close to unity for both the gas and liquid phase interface.

In a similar vein, the CO molecule/H atom ratio measured by both gas-phase and electrochemical methods is less than unity, lying between 0.8 and 0.9. The data of Table 3 indicate that the sharp decrease in CO/H noted by Freel for platinum crystallites greater than about 60 Å on oxide supports, was not apparent in the present catalysts. In the gas phase, for crystallites up to about 110 Å diameter (Table 2, 20% Pt), and by the electrochemical method, for platinum crystallites up to 220 Å, (Table 3, platinum black) the CO/H ratio did not fall below about 0.8. In all other respects, platinum supported on carbon was similar to platinum on oxide supports, whether observed by gas-phase or electrochemical measurements.

Since the gas phase and electrochemical measurements yield similar results for stoichiometry of hydrogen and carbon monoxide chemisorption, the additional information yielded by the electrochemical measurement should also be relevant to the gas phase systems. Thus, the electrochemical measurement with no additional experimental effort, gives not only the quantity of hydrogen adsorbed, but also the relative quantities of hydrogen in strongly and weakly bound states. These have been related to adsorption on specific crystallographic faces of platinum and indeed the ratios of these peaks change on platinum samples of different morphology or pretreatment history. Furthermore, the oxidation of adsorbed CO need not necessarily give a simple oxidation peak but would be expected to be resolved into peaks reflecting different bonding states. In fact, the CO oxidation peak of Fig. 4, though shown as a single peak, frequently is resolved to give the appearance of a shoulder at lower potentials. Stonehart (*19*) has recently explained this additional peak, for less than 50% coverage with CO, as due to the surface interaction of adsorbed CO with coadsorbed water molecules. The occurrence of two peaks, in the absence of adsorbed hydrogen, suggests two surface states of CO and indicates the need for further study.

The increased resolution of the energy states of the adsorbed species, as well as the rapidity of the measurement, and the effectiveness of electrochemical oxidation procedures for cleaning the catalyst surface render electrochemical techniques as an attractive complementary approach for the study of platinum-on-carbon systems.

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