PLATINUM CATALYSTS SUPPORTED ON GRAPHITIZED CARBON BLACK—I

CHARACTERIZATION OF THE PLATINUM BY TITRATIONS AND DIFFERENTIAL CALORIMETRY

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Abstract—A graphitized carbon black and samples resulting from its oxidation in air at 798 K over different periods of time have been used as supports for platinum catalysts. Platinum dispersion and mean diameter of platinum particles have been determined by O₂–H₂, H₂–O₂ and O₂–CO titrations and by differential calorimetry of the O₂–H₂ reaction. Comparison of titration results does not permit an unambiguous choice of Pt/O or Pt/CO ratios to be used in the titration stoichiometries. However, results from the calorimetric study suggest that the Pt/O ratio should be taken as one. Dispersion increases with increasing burn-off of the support; the surface area of the support being the principal factor conditioning the platinum dispersion, although there is also a smaller contribution due to the increase in surface heterogeneity.

1. INTRODUCTION

Carbon blacks are being used as catalyst supports for some applications because of their relatively high electrical conductivity and low chemical reactivity of their surface[1–5]. Bartholomew and Boudart[2], Ehrburger et al.[4] and Ehrburger and Walker[5] have used carbon blacks (Graphon and Vulcan 3G) as catalyst supports and have investigated the effect of carbon black activation on the degree of dispersion (which is defined as the ratio of metal surface atoms to the total number of metal atoms in the catalyst) of the catalyst. Ehrburger et al.[4] conclude that the increase in the degree of dispersion of the catalyst with support activation is due to an increase in surface area and, especially, in heterogeneity of the support. However, there is not yet any systematic study of the changes in surface properties (such as surface area, porosity and surface heterogeneity) of a carbon black used as a support upon its activation and the relation of these properties to the final characteristics of the catalysts prepared.

Taking into consideration these facts, we have conducted a study in which platinum catalysts have been prepared using a graphitized carbon black (Vulcan 3G) with different degrees of activation of the support. Characterization of the support can be found elsewhere[6]. Characterization of the catalysts using a wide range of experimental techniques will constitute this and the following paper in an attempt to relate the surface characteristics of the support to those of the catalysts and to analyze the different methods which can be used to study metal catalysis supported on carbon.

In this first paper on the characterization of the catalysts, special attention is given to the now classical method of the titration of a chemisorbed gas[7] on the surface of platinum and also to the differential calorimetry of the O₂–H₂ reaction.

2. EXPERIMENTAL

2.1 Materials

Five platinum catalysts have been prepared following the impregnation technique (chloroplatinic acid dissolved in a mixture of benzene and absolute ethanol) described elsewhere[2]. Platinum contents ranged in all cases from 0.8 to 0.9% by weight as determined by both neutron activation and gravimetric analysis (that is, by burning away the carbon).

The supports used were a graphitized carbon black (Vulcan 3 (V3G)) and four samples resulting from activation of the above support; activation was carried out by gasification in high purity dry air at 798 K for different periods of time. Surface characteristics of the supports have been described in a previous paper[6]. The description of the five catalysts prepared is presented in Table 1. The number appended to V3G gives the percent carbon weight loss during sample activation.
Reduction of the samples, prior to titration, was carried out in situ in the volumetric chemisorption system following the procedure of Benson and Boudart[7] slightly modified, i.e. 16 hr at 773K in a flow of H₂ followed by outgassing for 1 hr. These experimental conditions have been selected in order to compare the results with others obtained under these conditions[4].

### 2.2 O₂-H₂ Titration

Once the sample was reduced and evacuated and brought to the temperature of 303K, it was exposed to 101 kPa of O₂ for 1 hr and evacuated for 1 hr to 133 μPa. Then, titration of the chemisorbed oxygen was carried out with H₂ at 303K. Water vapor released during the titration may not be completely adsorbed by the V3G support[4]; and, therefore, in order to ensure that all the evolved water vapor was adsorbed, Drierite (CaSO₄) was used. The Drierite was not directly mixed with the supported catalyst as in other works[4] because of the reduction temperature used (at 773K, CaSO₄ and carbon may react to give CuS) but was placed beside the catalyst.

In addition to the titration reactions, the adsorption of hydrogen on the supports was studied using the same temperature and pressure range as in the O₂-H₂ titrations.

### 2.3 H₂-O₂ Titration

This is the reverse of the above reaction and it has been carried out under the same experimental conditions. In this case, the adsorption of oxygen on the supports was studied before carrying out the corresponding titration reaction on the catalysts.

### 2.4 O₂-CO Titration

This reaction, described by Wentrcek et al.[8], is based on the reaction of oxygen chemisorbed on the surface of platinum particles with CO. The reaction was carried out in the same volumetric system used for the O₂-H₂ and H₂-O₂ titrations[1]. Once the catalyst was reduced and outgassed for 1 hr at 773K, it was cooled down to 303K under vacuum. Then it was exposed to 101 kPa of O₂ for 1 hr. After this period of time, the sample was outgassed at 303K for 1 hr to 133 μPa. The chemisorbed oxygen was titrated using successive doses of CO, allowing a contact time of 1 hr for each dose. A liquid nitrogen trap, placed beside the adsorption system, removed CO₂ produced during the titration.

As in the case of the O₂-H₂ titration, a second adsorption run of CO on the catalysts was carried out after the O₂-CO titration. Once the titration was completed, the sample was outgassed at 303K for 16 hr to 133 μPa and then the adsorption of CO was measured.

The physical adsorption of CO on the support was measured. The treatment of the support prior to the adsorption runs was exactly the same as used during titrations.

### 2.5 Differential calorimetry

This technique can yield information about the amount of heat evolved during the reaction of hydrogen with the oxygen chemisorbed on the platinum of the catalysts[9]. A DuPont differential scanning calorimeter (DSC) attached to a 900 Thermal Analyzer has been used in this study. A complete description of this calorimeter can be found elsewhere[9, 10].

The samples were reduced in the volumetric chemisorption system, following the procedure described previously; then, oxygen was chemisorbed at 303K and the resulting sample was taken to the DSC. The basic problem found was to evacuate the reactor in order to eliminate the residual air. This problem was solved by using a pressure cell instead of the conventional one and carrying out several vacuum and helium dosing cycles[11]. The reaction was studied at 303K and the heat evolved, when H₂ (at a pressure of 1.37 MPa) was substituted for helium (1.37 MPa), was monitored as a function of time and sample temperature. The catalyst weight used was around 5 mg and always the corresponding support was used as the reference material.

Some blank runs were carried out to determine the heat of adsorption of hydrogen on the supports using an empty aluminum pan as reference material. Under the experimental conditions used, with the maximum sensitivity of the system (1.65 × 10⁻³ mJ/s mm), there was no heat of adsorption detected. However, when the catalyst was placed in the system and the corresponding support was used as reference material, a curve of the type shown in Fig. 1 was obtained, which corresponds to the heat evolved during the hydrogenation of the oxygen chemisorbed on the platinum surface of the catalyst. Although the shapes of the curves were very similar for the five catalysts studied, the corresponding areas under the curves were different. The reproducibility of the results was tested on two catalysts (V3G-O and V3G-9.3) by repeating the determination three times for each one. The areas measured were reproducible within ±2.5% for each catalyst. Calculation of the heat of reaction from the

### Table 1. Surface areas of carbon substrates and platinum loading on them

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m²/g)</th>
<th>Pt Content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V3G-0</td>
<td>62</td>
<td>0.81</td>
</tr>
<tr>
<td>V3G-9.3</td>
<td>75</td>
<td>0.91</td>
</tr>
<tr>
<td>V3G-24.6</td>
<td>94</td>
<td>0.78</td>
</tr>
<tr>
<td>V3G-52.8</td>
<td>121</td>
<td>0.87</td>
</tr>
<tr>
<td>V3G-75.2</td>
<td>136</td>
<td>0.91</td>
</tr>
</tbody>
</table>
areas under the curves was carried out following the procedure described elsewhere [12].

3. RESULTS AND DISCUSSION

3.1 O$_2$-H$_2$ Titration

Adsorption of hydrogen on the supports was carried out at 303K and up to about 40 kPa pressure (conditions used during the O$_2$-H$_2$ titration). Equilibration on the supports was rapid, with all experimental adsorption points falling on straight lines which could be extrapolated to the origin. Figure 2 shows, as an example, the adsorption isotherm for hydrogen on the V3G-0 support.

One problem found when carrying out the O$_2$-H$_2$ titration was related to the equilibrium time. When the first dose of H$_2$ was admitted to the system, equilibrium was not reached rapidly as reported with other catalysts [7]. It required around 24 hr for equilibrium to be reached in the case of the V3G-0 catalyst. However, once equilibrium was reached for the first titration point, successive doses attained equilibrium in a few minutes, the volume of H$_2$ consumed being almost constant and independent of the H$_2$ pressure. On the other hand, this volume of H$_2$ consumed (after subtraction of the amount adsorbed on the support) corresponds to a degree of dispersion of platinum which is much greater than unity, or is unrealistic.

As a result of these findings, the titration reaction was carried out using different periods of time for contact between the catalyst and H$_2$, without waiting for equilibrium. Results for the V3G-0 catalyst using 1, 3 and 6 hr of contact time are shown in Fig. 2. For each period of time, the experimental points fall on a straight line which can be extrapolated to the ordinate. It is noted that for a contact time of 6 hr, the fourth experimental point (equivalent to a cumulative time of 24 hr) does not fit the straight line, but it is coincident with the isotherm obtained under equilibrium conditions (about 24 hr). This finding and the fact that the three lines (1, 3 and 6 hr) have the same intercept may be taken as an indication that during titration there is a fast consumption of hydrogen as indicated by some authors [13] which is almost independent of the H$_2$ pressure (provided it is high enough to form a monolayer) and of the contact time (provided this is the same for all the experimental points of the isotherms). For this reason, the intercept has been taken as the volume of H$_2$ consumed in the O$_2$-H$_2$ titration on the platinum, using in all cases a contact time of 1 hr.

If the intercept is taken as the volume of H$_2$ consumed in the titration, no correction is needed for adsorption on the support alone, since this adsorption is given by a straight line which extrapolates to the origin (see Fig. 2). That this is true will be confirmed below and when studying the H$_2$-O$_2$ titration described in the next section.

As seen, the adsorption of hydrogen on the support alone is very low, but results are very different with the catalysts, since the total amount of H$_2$ consumed is much larger than that taken here as needed for the titration, namely, the intercept (see Fig. 2). Thus, it is apparent that platinum dissociates hydrogen molecules; and consequent spillover of atomic hydrogen from the metal to the support is taking place. This phenomenon, which is rather common during titration of chemisorbed oxygen on carbon supported catalysts at 523K and above [14, 15] has not been reported previously for titrations near ambient temperatures [4]. However, Bott et al. [3] have described a slow uptake of hydrogen when studying hydrogen chemisorption on a platinum catalyst supported on a Vulcan XC-72 carbon black.

To obtain further insight into the nature of this hydrogen spillover at room temperature, further studies were carried out on selected catalysts. Once the titration reaction was completed, samples were outgassed at 303K for 16 hr and then a hydrogen adsorption run was carried out at the same temperature. Results obtained in these hydrogen adsorption runs have been included in Fig. 3 together with those corresponding to the initial titrations. Data for the adsorption runs fall straight lines which can be extrapolated to the origin and which run parallel to straight lines depicting the original titration results. If instead of using a contact time of 1 hr, other times such as 3 or 6 hr are used, results found were totally coincident.

Outgassing at 303K for 16 hr, following hydrogen titration, is expected to remove hydrogen which is weakly bound to the platinum surface [13, 16, 17]. In addition, some or all of the hydrogen bound to the carbon support is expected to be removed [18, 19]. Data from the subsequent hydrogen adsorption runs, seen in Fig. 3,
suggest that hydrogen bound to the carbon support is essentially all removed by outgassing at 303K. That is, the lines depicting the adsorption runs are parallel to those depicting the titration runs. In agreement with the findings of Robell et al. (1), we conclude that the slow uptake of hydrogen on platinum carbons is due to activated diffusion of weakly adsorbed hydrogen atoms away from platinum centers which chemisorb molecular hydrogen rapidly. The slow process is also a reflection of the probability that hydrogen atoms will collide and recombine while diffusing across the carbon surface and leave the surface as molecular hydrogen, prior to their reaching and chemisorbing on active carbon sites. All this seems reasonable since, as it will be shown in the next section, slow adsorption and spillover are not observed in the reverse \( \text{(H}_2\text{O}_2) \) titration where it is understood[12] that there is only oxygen tightly bound to the platinum surface atoms at 303K.

As seen in Fig. 3, the amount of \( \text{H}_2 \) taken up in the adsorption runs increases from the sample V3G-0 to V3G-74.2. This may be explained by: (i) an increase in surface area and heterogeneity of the support upon increasing activity[6], which can lead to an increase in the extent of hydrogen chemisorption on the support and/or (ii) an increase in the amount of weakly held hydrogen with an increase in platinum dispersion.

The method used here to determine the amount of hydrogen consumed in the titration as that given by the intercept (Fig. 3) does correct for the hydrogen adsorbed on the support as a consequence of spillover without need to measure it. In fact, the difference between both isotherms should give a Langmuir type isotherm whose flat portion would give the amount of hydrogen consumed rapidly in the \( \text{O}_2\text{-H}_2 \) titration as deduced by extrapolation to zero pressure (see Fig. 3). This procedure does not account for the hydrogen weakly bonded to platinum sites, that is hydrogen which does not remain on platinum sites during the early stages of titration because of spillover.

Once the amount of hydrogen used in the titration is known, a stoichiometry is needed to determine the number of platinum atoms at the surface or the degree of dispersion. There are different stoichiometries that can be used in the \( \text{O}_2\text{-H}_2 \) titration[20, 21]. The two which will be used here are:

\[
\text{Pt}(O) + \frac{3}{2} \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{Pt}(H) \quad (1)
\]

and

\[
\text{Pt}_2(O) + 2 \text{H}_2 \rightarrow \text{H}_2\text{O} + 2 \text{Pt}(H). \quad (2)
\]

Some of the data obtained in the \( \text{O}_2\text{-H}_2 \) titrations are summarized in Figs. 4 and 5. It is clearly shown that the characteristics of the catalysts such as the mean diameter of the platinum particles (assuming spherical shape) and the degree of dispersion vary with the degree of burn-off of the support, i.e. the degree of platinum dispersion is about three times larger in sample V3G-74.2 than in V3G-0.

According to Ehrburger et al.[4], the increase in platinum dispersion cannot be explained in terms of total surface area increase of the support as a result of gasification but is due to an increase in the surface heterogeneity. However, a detailed analysis of their

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**Fig. 3.** \( \text{O}_2\text{-H}_2 \) titrations (open circles) and subsequent hydrogen adsorption runs (closed circles) on selected catalysts. A constant time of 1 hr was used.

**Fig. 4.** Change in platinum dispersion and mean particle diameter with extent of activation of carbon support as measured by titrations. Stoichiometry assumed: reactions (1) and (3), open symbols and reactions (2) and (4), closed symbols.
results (for instance, the calculation of surface platinum atoms per unit area) can show that in all samples but one (the most highly gasified) the increase in platinum dispersion corresponds almost exactly to the increase in total surface area of the support. In the present study, the number of surface platinum atoms per unit area of support is almost constant and independent of the extent of burn-off given the support, as seen in Fig. 5.

3.2 \( \text{H}_2\text{-O}_2 \) Titration

The \( \text{H}_2\text{-O}_2 \) titration, although not commonly used [13], may prove helpful in obtaining some additional information about the carbon supported catalysts. As in the previous titration, it was necessary to measure adsorption of the titrating gas on the supports. Uptake was rapid, equilibration occurring within 30 min. Adsorption isotherms of \( \text{O}_2 \) at 303K on the supports (see Fig. 6 for some examples) were again straight lines, but the lines do not extrapolate to the origin. Rather they show a positive intercept; meaning that a correction for \( \text{O}_2 \) adsorbed on the support is needed. The \( \text{H}_2\text{-O}_2 \) titration reaction is rapid; equilibrium was reached within 1 hr for the first experimental point and within 10 min for subsequent adsorption points. This suggests that little spillover of oxygen atoms from the platinum onto the support surface occurs at 303K.

The positive intercept of the isotherms for adsorption on the support suggests that dissociative chemisorption of oxygen on to active sites on the supports is occurring, in addition to physical adsorption. This conclusion is consistent with previous studies, which show oxygen chemisorption on graphitized carbon blacks at room temperature to be rapid [22]. Comparison of results for the V3G-0 samples given in Figs. 2 and 6 are interesting. From the intercept of the oxygen isotherm on this support, given in Fig. 6, it is seen that about 0.01 cc \( \text{O}_2 \) (STP) g\(^{-1}\) support is chemisorbed at 303K. Assuming that the oxygen is dissociatively chemisorbed on to carbon active sites, with one oxygen atom per active site, and that each active carbon site occupies 0.083 nm\(^2\) [22], it is calculated that the active surface area is about 0.044 m\(^2\) g\(^{-1}\) or active sites occupy about 0.032\% of the total surface area of the V3G-0 sample. This is consistent with the surface of graphitized carbon blacks being highly homogeneous and being composed almost entirely of basal plane surfaces of carbon crystallites [23, 24].

From Fig. 2, it is seen that the amount of hydrogen chemisorbing on the V3G-0 support from molecular hydrogen is still smaller than the amount of oxygen chemisorbing; it could not be measured. This is consistent with previous findings that hydrogen dissociatively chemisorbs onto only a fraction of carbon sites which chemisorb oxygen dissociatively [25]. In contrast, hydrogen pick-up on the support via spillover is much larger than the amount of oxygen chemisorbed on the support. That is, from Fig. 2, if the amounts of hydrogen consumed in the rapid titration reaction and physical adsorption are subtracted from the total hydrogen uptake at equilibrium, it is estimated that 2 cc \( \text{H}_2 \) (STP) g\(^{-1}\) support slowly spill over from the platinum onto the carbon support. This result suggests that hydrogen atoms are chemisorbing on carbon sites which are accessible to but do not dissociatively chemisorb oxygen and/or hydrogen atoms can differ along crystallite procedures in the V3G-0, unaccessible to either molecular hydrogen or oxygen, and chemisorb.

Results obtained from the \( \text{H}_2\text{-O}_2 \) titrations are given in Figs. 4 and 5, using stoichiometries given by the following equations

\[
2 \text{Pt(H)} + \frac{3}{2} \text{O}_2 \rightarrow \text{H}_2\text{O} + 2 \text{Pt(O)}
\]

\[
2 \text{Pt(H)} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Pt}_2\text{(O)}
\]

Oxygen is expected to titrate hydrogen strongly bound to the platinum surface, that is, that remaining after out-
gassing at 303K for 1 hr, following initial hydrogen chemisorption.

Figure 4 shows that the degree of dispersion of platinum increases with burn-off of the support in a very similar way when either the O₂-H₂ or H₂-O₂ titrations are used to follow changes. The number of surface platinum atoms per unit total area of support varies little with the amount of activation given the support, suggesting again that the principal factor influencing the increase in platinum dispersion is the total surface area of the support.

The results obtained in the two titration techniques used here, which are nearly coincident for each stoichiometry, show the validity of the assumptions made in both cases, but leave an uncertainty as to whether the oxygen to platinum ratio is O/Pt = 1 or O/Pt = 0.5.

3.3 Differential scanning calorimetry

Although the results obtained using the two titration techniques were nearly coincident, a further test was carried out by measuring the amount of heat evolved during hydrogenation of the oxygen chemisorbed on the platinum catalysts at the same temperature used in the titrations, that is 303K.

Figure 7 shows that the heat produced by the rapid O₂-H₂ titration, per unit weight of platinum, increases sharply with increasing burn-off (activation) given the carbon support. Figure 7 also shows that the heat produced, per unit weight of platinum, increases linearly with increase in specific surface area of the carbon support. It is expected that these correlations are a function also of the level of loading of platinum on the carbon supports. In this study the level of loading for all supports was closely similar, that is about 0.80–0.90% platinum. Ehrburger et al. [4] have shown that the extent of platinum dispersion not only increases as activation of the carbon support increases but also as the level of platinum loading decreases.

Figure 8 shows essentially a linear relationship between the variation in platinum dispersion (using reaction 1), as produced by using carbon supports activated to different degrees, and the heat of the O₂-H₂ titration, per unit weight of platinum. As expected, as the degree of dispersion goes to zero, the heat of titration per unit weight of platinum approaches zero. It would be interesting to see if this is a universal plot for the platinum-carbon system independent of the particular physical structure of the carbon used as support and the degree of platinum loading.

Figure 8 can be converted to the ΔH for the reaction of 1 mole of H₂ as a function of degree of platinum dispersion, assuming stoichiometry for the O₂-H₂ titration to be given by either reactions (1) or (2). Figure 9 shows results when reaction (1) is assumed. Enthalpies range from a low of -138 to a high of -205 kJ/mole H₂. No systematic trend with change in degree of platinum dispersion is observed. If reaction (2) is assumed to be operative, calculated enthalpies for the O₂-H₂ titration reaction range between -207 and -308 kJ/mole H₂.

Some guidance as to which stoichiometry is operative in the O₂-H₂ titration can be obtained if the experimental enthalpies are compared with enthalpies predicted from heats of reaction. Reactions to be considered are

\[
\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H = -242.7 \text{ kJ/mole H}_2
\]  

(5)

\[
\text{H}_2\text{O}(g) \rightarrow \text{H}_2\text{O}({\text{ads}}) \quad \Delta H = -46.0 \text{ kJ/mole H}_2\text{O}
\]  

(6)

\[
\text{H}_2(g) + 2 \text{Pt} \rightarrow 2 \text{Pt(H)} \quad \Delta H = -71.1 \text{ kJ/mole H}_2
\]  

(7)

\[
\frac{1}{2} \text{O}_2(g) + \text{Pt} \rightarrow \text{Pt(O)} \quad \Delta H = -209 \text{ kJ/mole O}_2
\]  

(8)

\[
\frac{1}{2} \text{O}_2(g) + 2 \text{Pt} \rightarrow \text{Pt}_2(\text{O}) \quad \Delta H = -200 \text{ kJ/mole O}_2
\]  

(9)

If the O₂-H₂ titration is assumed to be given by reaction (1), ΔH for the titration is -150 kJ/mole H₂. If reaction (2) is assumed to be operative, ΔH for the titration is -130 kJ/mole H₂. Internal consistency between experiment and theory is found if reaction (1) is assumed to be operative; it is not found for reaction (2). That is, in the
latter case the calculated $\Delta H$ (130 kJ/mole H$_2$) falls outside of the $\Delta H$ range found experimentally.

There are uncertainties as to exact values which should be taken for enthalpies of some of the individual reaction steps given above and further whether all reaction steps are necessary. When the titration run was conducted in the DSC, no special adsorbent for the water formed was present. All water formed may not have adsorbed on the catalyst surface, as was assumed in the enthalpy calculation. A considerable range of experimental values exist for heats of chemisorption of hydrogen and, particularly, oxygen on platinum[36]. The value selected for reaction (7) is close to that recommended by a number of workers[27-30]. The value selected for dissociative chemisorption of oxygen on platinum (possibly given by either reactions (8) or (9)) was suggested recently from the studies of Gland[31].

3.4 O$_2$-CO Titration

Selected O$_2$-CO titrations are given in Fig. 10 for carbon supports ranging from no burn-off to 74.2% burn-off in air. The titration is rapid, equilibrium being reached in several minutes. This is to be compared to the O$_2$-H$_2$ titration, where equilibrium times up to 24 hr were required. This result would be predicted since dissociative chemisorption of CO on platinum at room temperature, with accompanying spillover of oxygen atoms on to the carbon support, is not expected.

Also shown in Fig. 10 are second adsorption runs for CO. Equilibrium in these runs is also rapid. Data points fall on straight lines running parallel to the lines describing the titration runs and pass through the origin. The lines are coincident with those obtained for adsorption of CO on the respective supports alone. Uptake is attributed, therefore, solely to physical adsorption on the carbon support. This result is consistent with previous findings that CO chemisorbed on platinum is tightly bound and cannot be removed by outgassing at room temperature[32]. Thus, the CO consumed in the titration reaction is given by the intercept obtained by extrapolation of the titration plots in Fig. 10 to zero pressure.

Once the amount of CO used in the titration is known, a stoichiometry is needed to determine the number of platinum atoms at the surface or the degree of dispersion. Unfortunately, the stoichiometry is in doubt because of the possibility of CO chemisorbing in either the linear or bridged form[32]. Further, Wentzrees et al.[8] conclude that the maximum CO surface coverage following the O$_2$-CO titration is CO/Pt equals 0.5, even though the Pt-CO bond is linear. That is, they conclude that only half of the platinum atoms are covered by CO. Assuming that the Pt/O ratio is one, the stoichiometries considered are

$$\text{Pt} + 2\text{CO} \rightarrow \text{Pt}(\text{CO}) + \text{CO}_2 \quad (10)$$

$$2\text{Pt} + 3\text{CO} \rightarrow 2\text{Pt}_3\text{(CO)} + 2\text{CO}_2 \quad (11)$$

in which the ratios of CO molecules consumed to the number of platinum surface atoms are 2 and 3/2, respectively. Reaction (11) may be taken to describe the case of either CO chemisorbing in the bridged form or one linear CO chemisorbing for each two platinum sites.

If the Pt/O ratio is two, the stoichiometries considered are:

$$\text{Pt}_2(\text{O}) + 3\text{CO} \rightarrow 2\text{Pt}(\text{CO}) + \text{CO}_2 \quad (12)$$

$$\text{Pt}_2(\text{O}) + 2\text{CO} \rightarrow 2\text{Pt}_2(\text{CO}) + \text{CO}_2 \quad (13)$$

Reactions (11) and (12) will yield the same results, that is 3/2 CO molecules are consumed for each platinum site.

Results for the degree of platinum dispersion and mean diameter of the platinum are summarized in Table 2. As found for the O$_2$-H$_2$ and H$_2$-O$_2$ titrations, the number of platinum surface atoms per unit area of carbon support is essentially independent of the degree of oxidation given the support; or platinum dispersion increases approximately linearly with increasing carbon surface. It is not possible on the basis of comparison of results for the O$_2$-CO titration with the O$_2$-H$_2$ or H$_2$-O$_2$
Table 2. Characterization of platinum on V3G carbon substrates from O₂-CO titration assuming different reaction stoichiometries

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Degree of Dispersion</th>
<th>Mean Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(10) (11.12) (13)</td>
<td>(10) (11.12) (13)</td>
</tr>
<tr>
<td>V3G-0</td>
<td>0.17 0.22 0.34</td>
<td>6.4 4.9 3.2</td>
</tr>
<tr>
<td>V3G-9.3</td>
<td>0.22 0.29 0.44</td>
<td>6.9 4.7 2.5</td>
</tr>
<tr>
<td>V3G-24.6</td>
<td>0.25 0.33 0.50</td>
<td>6.3 3.3 2.2</td>
</tr>
<tr>
<td>V3G-52.8</td>
<td>0.29 0.38 0.57</td>
<td>3.7 2.8 1.9</td>
</tr>
<tr>
<td>V3G-74.2</td>
<td>0.33 0.46 0.69</td>
<td>3.1 2.3 1.6</td>
</tr>
</tbody>
</table>

...tirations to select PtO or P/O ratios which give best agreement for platinum dispersion.

4. CONCLUSIONS

Various titration techniques show that the dispersion of platinum supported on graphitized carbon black is mainly determined by the surface area of the support, which is a function of the level of carbon burn-off. Differential scanning calorimetry is shown to be a simple technique which can be used to characterize platinum catalysts supported on carbons. However, all these results do not give a definite answer as to the appropriate PtO ratio which should be assumed in the stoichiometries and, therefore, lead to uncertainty as to absolute values of platinum dispersion and particle size. The following paper [34], which employs transmission electron microscopy and small angle X-ray scattering techniques, helps to resolve this matter.

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REFERENCES