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Chemisorption on Supported Platinum

I. Evaluation of a Pulse Method

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A flow method was used to measure hydrogen chemisorption on supported platinum catalysts. At ambient temperature, the data were in accord with results obtained by the conventional static method. Therefore, the stoichiometry of hydrogen chemisorption assumed in the conventional measurement was used to calculate platinum dispersion from the flow results. Electron microscope studies indicated that the pulse method provided a reasonable estimate of platinum dispersion ($0.2 \leq H/Pt \leq 1.0$) when used in this way. Some exceptions are pointed out.

Hydrogen uptakes at elevated temperatures (200–300°C) could not be treated in the same way. A substantial volume of hydrogen was reversibly chemisorbed at these temperatures, a quantity included in the conventional measurement but excluded from the flow determination.

Oxygen chemisorption and the titration of absorbed oxygen with hydrogen could also be followed conveniently at 25°C. These provided some useful tests of the flow procedure.

INTRODUCTION

Hydrogen and carbon monoxide chemisorption are commonly used to determine metal surface area in supported metal catalysts, since under appropriate conditions the metal will chemisorb these gases while the oxide support will not. Metal surface area may then be estimated, provided the stoichiometry with which the gas and metal interact is known. Originally this information was obtained by comparison of chemisorption with B.E.T. data for pure metals, but more recently, independent techniques such as electron microscopy and X-ray diffraction line broadening have confirmed the general utility of this approach (*1–3*). The interpretation of chemisorption on practical catalysts can be undertaken with some confidence as a result, and in principle, metal dispersion can be measured on a routine basis. The classic high-vacuum apparatus, however, is ill suited for such routine use.

Flow methods offer a simpler means for measuring chemisorbed volumes. In early applications (*4*), the catalyst was contacted with a flow of inert gas containing a small amount of adsorbate and the volume chemisorbed was measured from the time required for breakthrough of the adsorbate relative to a blank. As pointed out by Buyanova. Ibragimova and Karnaukov (*5*), however, the accuracy of these "frontal" methods is limited and modifications devised to improve accuracy (*6*, *7*) do so only at the cost of simplicity. The pulse adsorption method, first reported by Gruber (*8*), adopted a significantly different approach. Here a pulse of adsorbate was injected into the flow of inert gas and passed over the catalyst. As described by Gruber, the volume of adsorbate was measured before and after contact with the catalyst, and the volume adsorbed given by difference. In a subsequent modification (*10*), pulses were designed to be appreciably less, rather than more, of the anticipated uptake and were fully adsorbed until the monolayer was complete. Several fully eluted pulses were recorded at the end of the measurement and any partly adsorbed pulses were calibrated against these.

This last procedure has been used in a variety of recent studies. It seems necessary to emphasize, therefore, that chemisorption defined by these methods is different from that defined by conventional experiments. Although complete adsorption isotherms can be calculated from flow measurements (*9*), the simpler procedures described above measure only chemisorption which occurs rapidly and irreversibly. The static method, in contrast, allows time for equilibration and includes both reversible and irreversible adsorption. As a consequence, knowledge derived from conventional measurements, in particular the stoichiometry with which gas and metal interact, cannot automatically be transferred from the one to the other.

In the present study, pulse and conventional measurements were compared on several platinum–silica samples. The two were found to be in fair agreement, and consequently a model derived from static measurements was used to correlate hydrogen uptakes in the flow method with platinum crystallite size. Direct observation of platinum dispersion by electron microscopy suggested that this model was appropriate for a variety of supported platinum catalysts, but possible exceptions are pointed out.

Similar comparisons have been reported previously (*8*, *10*, *11*), but were restricted to one or two samples and the authors did not always agree in their conclusions. Roca, deMourgues and Trambouze (*10*), for example, used the pulse method to measure hydrogen adsorption on platinum at 200°C, while Buyanova *et al.* (*5*) concluded that this was not feasible.

EXPERIMENTAL

(a) **Apparatus.** Adsorption measurements were made in a modified Aerograph A-700 glc. The flow schematic is shown in Fig. 1. Catalyst was contained in ¼ in. o.d. stainless-steel tubing, approximately 8 in. long, which replaced the original glc column; all other tubing was ⅛ in. o.d. "Gyrolok" unions and adapters were used throughout. Hydrogen pulses were injected using a 6-port, O-ring type glc sample injector (Varian Aerograph), and a standard 4-port glc "back-flush" valve was used to change the flow through the catalyst between either of two gases. The other flowed through the sample loop of the injection valve as indicated in Fig. 1. Detector response was measured on an 0–10 mV, 12 in. recorder and calibrated rotameters were used to measure gas flow rates.

Procedural details have already been given (*5*, *10*). Gas flow rates (30–50 cc/min)

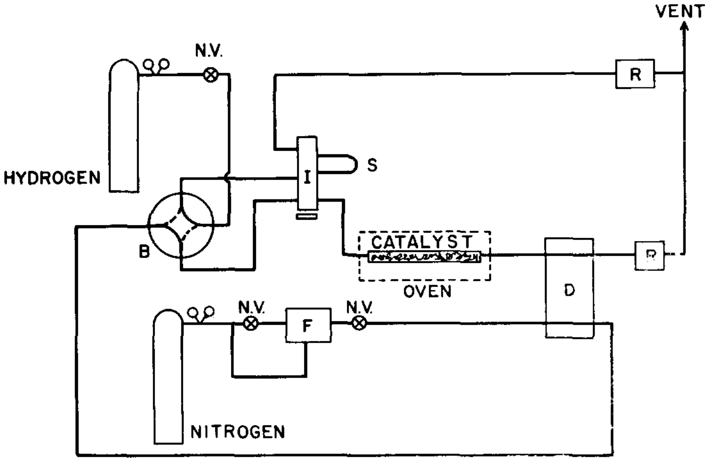

FIG. 1. Schematic of the flow system. F = "Moore" flow controller, N.V. = needle valve, D = thermal conductivity detector, B = glc backflush valve, I = 6-port "Varian" sample-injector, S = sample loop, R = rotameter. The setup for hydrogen adsorption is shown. Prereduction was carried out with the valve B in its alternate position. Oxygen chemisorption was studied by replacing the hydrogen source with oxygen.

and catalyst particle size (40–60 mesh) were chosen on the basis of Gruber's (*8*) study and catalyst pretreatment (one hour in hydrogen at 500°C followed by one hour in nitrogen at the same temperature) on the basis of experiment. Experiments also showed that raising the temperature slowly (4°/min) to 500°C during reduction was less likely to alter platinum dispersion and thus afforded better reproducibility.

The relationship of injected volume to catalyst weight is somewhat arbitrary. However, it is desirable to keep the catalyst sample within reasonable limits, to inject volumes of adsorbate such that detector response is linear within that range, and to balance the two so that four or five injections are required to saturate an average sample. A catalyst weight of 1.5–3.0 g and an injected volume of approximately 0.25 cc (STP) was adopted in the present study.

(b) **Calibrations.** Clearly the volume injected must be known accurately. Since the injection valve used had an appreciable dead volume, five $\frac{1}{16}$ in. o.d. stainless-steel sample loops were constructed with volumes encompassing the range of interest (0.05–0.40 cc STP). Their volumes were obtained by filling with mercury and a loop-volume vs detector response calibration obtained. The calibration was linear with peak area and gave a negative intercept on the loop-volume axis corresponding to the dead volume of the valve (0.19 cc (STP)). A maximum error of ±4% in the total volume injected was estimated graphically and detector response tests indicated that this fixed volume could be injected with a reproducibility better than ±1%.

(c) **Materials.** Most of the catalysts used in the present study were made by impregnation with chloroplatinic acid using the incipient wetness technique, a few by a chemideposition method. All platinum-on-alumina samples were prepared using Sinclair–Baker η-alumina, all platinum-on-silica samples using Davison Grade 70 silica gel. Platinum contents were determined by an X-ray fluorescence method.

The gases used were "ultrapure" hydrogen and "research grade" oxygen (Matheson Gas Products). "Carrier Grade" nitrogen, which was supplied by Air Products and Chemicals Inc., contained about 1 ppm oxygen and <1 ppm water. All gases were used without further purification.

(d) **Electron microscopy.** Catalyst samples were crushed in a mortar and pestle, immersed in an inert solvent, and fine ground in a ground-glass joint. The resulting suspension was sprayed onto "holey" carbon films, predeposited on standard copper grids. Samples were examined at 100 kV in a Phillips EM-300. Thin catalyst particles, lying over holes in the mounting film, were photographed at 250,000× magnification. The resulting micrographs were enlarged 4× and some 300–400 platinum crystallites sized per sample. Platinum crystallites smaller than 10 Å have been resolved using this procedure. Platinum–alumina samples were stable in the electron beam. At full illumination, silica fused slowly. Therefore, platinum–silica samples were photographed rapidly at minimum useful illumination. Melting of the silica did not seem to have a significant effect on platinum crystallite size, the crystallites presumably being included in the collapsing micropore structure. Nevertheless micrographs showing evidence of silica fusion were discarded.

RESULTS

(a) **Hydrogen chemisorption.** Recent work suggests that the stoichiometry of hydrogen adsorption on platinum is more constant than that of oxygen or carbon monoxide (*2*, *3*, *12*), and accordingly, hydrogen was selected for initial evaluation. Although previous studies of hydrogen adsorption by the pulse method were carried out at 200°C (*10*) and 300°C (*13*), preliminary measurements were made at 25°C, since it seemed reasonable to assume that reversible adsorption on platinum would be smaller at room temperature.

Pulses were adsorbed rapidly at 25°C as at 200°C (*10*). There was no hydrogen breakthrough until saturation occurred, at which time one or two partly adsorbed pulses preceded complete elution. The latter pulses, showed pronounced tailing. This is illustrated in Fig. 2 which compares hydrogen pulses after passage through a platinum–silica catalyst and through a sample of silica alone. Hence, even at 25°C, a part

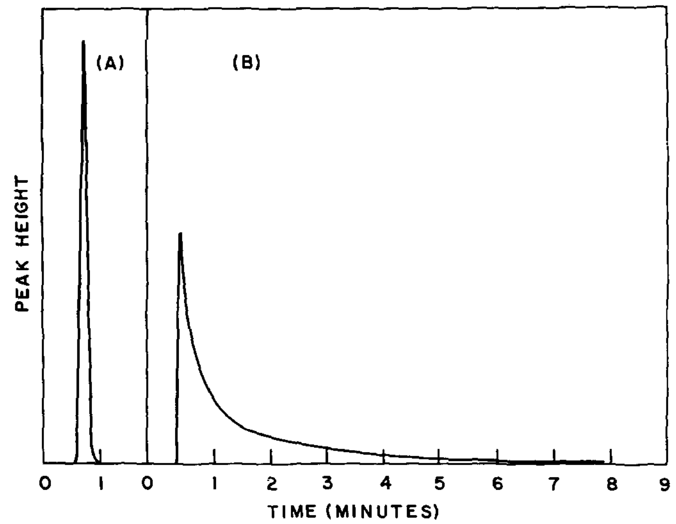

FIG. 2. Detector response for an 0.461 cc STP pulse of hydrogen (A) after passage through silica alone (attenuation 8×), and (B), after passage through an equivalent amount of 3.6% platinum-silica when the monolayer was complete (attenuation 2×). The nitrogen flow rate was 20 cc/min and six such pulses were irreversibly adsorbed prior to (B).

of the hydrogen has a substantial residence time on the platinum due to a weak, reversible form of hydrogen adsorption. With care, the shape of these peaks can be used to formulate a complete adsorption isotherm (*9*), but in the present study, the phenomenon was used only as a qualitative indication of reversible adsorption.

Static adsorption measurements were not made in this study, but the gift of platinum–silica catalysts, well characterized by conventional measurements, made a direct comparison possible. Thus the data of Wilson and Hall (*14*) are compared with values obtained in the present work in Table 1, a comparison which indicates that hydrogen uptakes at 25°C measured by the present method were equivalent to those obtained from the zero pressure intercepts of equilibrium isotherms.

As the adsorption temperature was raised, the volume of strongly bound hydrogen decreased and a concomitant increase in reversible adsorption occurred.

TABLE 1
COMPARISON OF CONVENTIONAL MEASUREMENTS[a] WITH THOSE OBTAINED BY THE FLOW METHOD

	Hydrogen uptake (atoms × 10^{-19}/g catalyst)		Oxygen uptake (atoms × 10^{-19}/g catalyst)		Hydrogen required for titration of adsorbed oxygen (atoms × 10^{-19}/g catalyst)	
Catalyst notation	Wilson[a] and Hall	Present study	Wilson[a] and Hall	Present study	Wilson[a] and Hall	Present study
3.6% Pt/SiO_2[b]	10.72	10.50	6.28	6.16	24.17	24.94
3.6% Pt/SiO_2[b]	9.78	9.83	5.94	6.75	22.81	24.13
2.8% Pt/SiO_2[c]	4.53	4.41	2.98	2.91	10.85	10.70

[a] G. R. Wilson and W. K. Hall—unpublished results.

[b] Prepared by the chemideposition method of Benesi, Curtis, and Studer (*23*).

[c] Prepared by impregnation with chloroplatinic acid.

For example, an 0.7 wt % platinum–alumina, which took up 1.22×10^{19} hydrogen atoms/g at 25°C, took up only 0.31×10^{19} hydrogen atoms/g at 300°C. On cooling to 25°C immediately after the latter determination, the sample took up a further 0.94×10^{19} hydrogen atoms/g.

Any correlation of hydrogen chemisorption and platinum dispersion is more simply achieved if its assumptions have general acceptance. Thus while the flow uptakes at elevated temperatures are probably related to dispersion, further work was confined to chemisorption at 25°C. Such uptakes were compared to platinum size distributions obtained from electron micrographs, catalysts being given a variety of posttreatments to provide a suitable range of dispersion. As pointed out by Moss *et al.* (*15*, *16*) platinum–silica catalysts are particularly pliable in this respect. Consequently, a large part of the study was carried out using platinum–silica catalysts. A few platinum–alumina catalysts were included for comparison. Excellent dispersions ($H/Pt \sim 1$) were obtained by careful reduction of silica samples prepared by a chemideposition method, moderate values ($H/Pt \sim 0.5$) from samples made by impregnation with chloroplatinic acid, and relatively low values ($H/Pt \sim 0.2$) from catalysts fired in air prior to reduction.

Catalysts were examined in the electron microscope immediately after the hydrogen adsorption measurements. Several hundred platinum crystallites were sized for each sample, and the resulting size distributions used to calculate surface average diameters, $\Sigma n_i d_i^3/\Sigma n_i d_i^2$ where n_i is the number of crystallites in a suitable increment of diameter whose mean is d_i. Surface areas were obtained from these mean diameters assuming spherical geometry.

$$\text{Area} = \frac{6 \times 10^8}{p \times d} \text{ cm}^2/\text{g platinum},$$

where p is the density of platinum and d the mean diameter in Å. (In fact, the crystallites appeared to be cubo-octahedral when large enough to distinguish shape, but this relationship applies for all regular polyhedra except the tetrahedron.) The number of surface platinum atoms in each sample was then calculated assuming a surface atom density of 1.12×10^{15} platinum atoms/cm², an average of those for the (1,0,0) and (1,1,0) planes (*17*).

The above calculation of surface area is equivalent to an integration of area over the size distribution. It is readily shown that for spheres of diameter d,

$$d = \frac{6 \times 1/6\pi d^3}{\pi d^2} = \frac{6V}{A}$$

where V is the volume of one such sphere, and A its surface area. With a distribution of sizes in i categories, therefore, the mean diameter $\bar{d}$ is given by

$$\bar{d} = (6\Sigma v_i)/(\Sigma a_i)$$

where v_i and a_i are the volume and area of each category. Thus

$$\bar{d} = \frac{6\Sigma 1/6 n_i \pi d_i^3}{\Sigma n_i \pi d_i^2} = \frac{\Sigma n_i d_i^3}{\Sigma n_i d_i^2}.$$

In Table 2, values of Pt_s/Pt calculated in this way are compared to the H/Pt values obtained by chemisorption, and the deviation from a 1:1 correspondence of the two is shown. Two of the resultant H/Pt_s values are appreciably greater than unity. However, any discrepancy between H/Pt and Pt_s/Pt is magnified in calculating H/Pt_s. The general agreement between the former quantities in columns 3 and 5 of Table 2, on the other hand, is probably within experimental error and, on this basis, the adsorption data appear to provide an acceptable estimate of platinum dispersion. A substantial uncertainty is associated with direct methods of estimating the mean crystallite size, in particular, and also with methods of calculating the number of surface platinum atoms for any given size.

The data of Table 2 were obtained with catalysts which had not been exposed to poisons such as sulfur. The method did not yield reliable data for such catalysts, even when severe oxidations were incorporated in the pretreatment. In all cases, the hydrogen taken up was substantially lower than the mean crystallite size would require.

The catalysts of Table 2 also contained at least 2 wt % platinum, primarily because

TABLE 2

Comparison of Hydrogen Sorbed at 25°C with Electron Microscopy

Sample	Pretreatment	H/Pt	Mean size from size distribution (Å)	Pt_s/Pt	H/Pt_s
2% Pt/SiO_2[a]	Oven dried 120°C Reduced 1 hr 500°C	0.98	14	0.73	1.34
2.8% Pt/SiO_2[b]	Oven dried 120°C Reduced 1 hr 500°C	0.36	32	0.32	1.13
1.83% Pt/Al_2O_3[b]	Oven dried 120°C Calcined 500°C Reduced 1 hr 500°C	0.89	12	0.85	1.05
2.0% Pt/SiO_2[a]	Oven dried 120°C Calcined 500°C Reduced 1 hr 500°C	0.24	40	0.25	0.96
2.0% Pt/SiO_2[a]	Oven dried 120°C Calcined 500°C Reduced 1 hr 500°C	0.19	85	0.13	1.46

[a] Prepared by chemideposition per Benesi, Curtis, and Studer (*23*).

[b] Prepared by impregnation with chloroplatinic acid.

it is difficult to obtain reliable size distributions when metal loading is low. Crystallites are much fewer in number, and it becomes difficult to decide when an opaque spot in the micrographs is a small platinum crystallite and when it is not. However, adsorption data for various 0.5% platinum–silica catalysts were found to be entirely consistent with the above picture and with conventional measurements. Carefully reduced samples prepared by chemideposition gave H/Pt values close to one, samples prepared by impregnation with chloroplatinic acid yielding substantially lower values. Results obtained with an 0.5% platinum–alumina catalyst were less encouraging. This sample had an H/Pt value of 0.6 after careful reduction. Conventional measurements would predict a value closer to one for this sample (*3*).

(b) **Oxygen adsorption.** Oxygen was also chemisorbed rapidly at 25°C and no reversible adsorption occurred, even at elevated temperatures. Pulses eluted on completion of the oxygen monolayer were identical to those obtained with only alumina or silica as adsorbent. As a consequence, oxygen adsorption could be measured more rapidly and more accurately than that of hydrogen, and the data obtained were once again in agreement with conventional measurements, as shown in Table 1. In these respects, oxygen was a particularly suitable adsorbate for use with the pulse method. However, as shown by Wilson and Hall (*3*) the stoichiometry of oxygen adsorption on platinum appears to vary, and therefore the estimation of platinum dispersion in this way would be difficult.

(c) **Hydrogen–oxygen titers.** Oxygen adsorbed on platinum will react with hydrogen at 25°C (*3*, *18*, *19*). This interaction and its counterpart, the reaction of adsorbed hydrogen with oxygen, were examined by the pulse method. They may be represented by the generalized equations,

$$\left(\frac{2x+y}{2}\right) H_2 + xO_* \rightarrow yH_* + xH_2O \ldots \quad \text{(i)}$$

$$\left(\frac{2x+y}{4}\right) O_2 + yH_* \rightarrow xO_* + (y/2)H_2O \ldots \quad \text{(ii)}$$

where H_* and O_* represent adsorbed atoms, H_2, O_2 and H_2O, gas phase molecules.

In the flow system, as in the static one (*18*), essentially all of the water formed and desorbed from the platinum is immediately readsorbed on the hydrophylic oxide support. Detector response indicated that some water escaped the catalyst towards completion of either reaction, but this did not interfere with the quantitative detection of hydrogen or oxygen. Thus, if oxygen or hydrogen were preadsorbed, gas uptakes for reactions (i) and (ii) could be followed exactly as though they were adsorption phenomena, hence the term "titer".

Each titer occurred rapidly enough to be followed quantitatively by the pulse method. In Table 1, for example, the hydrogen uptakes for reaction (i) were equivalent when measured by the two methods. The data given in Table 3 indicate a similarly quantitative interaction for a wider range of samples, since the following criteria were satisfied,

$$H_T = H_A + 2O_A, \qquad \text{(iii)}$$

$$O_T = O_A + 1/2H_A, \qquad \text{(iv)}$$

where H_T and O_T are the hydrogen and oxygen uptakes in titers (i) and (ii), respectively, H_A and O_A the uptakes on the bare surface. These equalities do not imply any stoichiometry to either adsorbed species, merely requiring that one adsorbate is removed quantitatively and replaced by the other in an amount equal to its own adsorption on the bare surface.

The pulse method was used to measure these titers on a variety of platinum catalysts. The data obtained will be published in detail subsequently, but certain aspects are germane to the present subject.

(1) The titration of adsorbed hydrogen with oxygen has no utility in conventional measurements. However, in the pulse procedure it can be utilized to obtain a large amount of data in a short period of time by measuring H_A, O_T and H_T sequentially at 25°C. In this way H_A, O_A [calculated from either Eqs. (iii) or (iv)], and H_T can be determined in approximately 40 min following the pretreatment of the sample. O_A calculated thus was equivalent to direct measurements of oxygen chemisorption as shown in Table 3.

(2) In the flow procedure, hydrogen adsorbed during reduction is removed by purging with an inert gas rather than by evacuation. The presence of strongly adsorbed impurities in this purge gas is a possible source of interference in all flow methods, and oxygen is the most likely offender when nitrogen is used. Oxygen gettered in this way would reduce the room temperature uptake of hydrogen on most transition metals. In the case of platinum, however, an increase in H_A must occur as indicated by Eq. (i). An error of this type would be difficult to detect if the only criterion used were comparison with conventional data, since H_A is likely to be smaller if anything in the pulse measurement. However, the ratio (H_A/O_A) forms a sensitive probe for oxygen content of the inert gas, because oxygen gettering will decrease O_A by some quantity δ, while increasing H_A by 2δ [see Eq. (i)]. Since the ratios H_A/O_A obtained in the present study agreed with those of Wilson and Hall (*14*) (Table 1), we may conclude that the hydrogen uptakes measured were not biased in this way.

(3) In some final tests, H_T and O_T were measured after treating the catalyst in flowing oxygen and hydrogen, respectively. The resulting titers were almost identical to those measured when oxygen and hydrogen were preadsorbed by pulsing. These results confirm that the rapid uptake of hydrogen or oxygen determined by the pulse method represents an equilibrium condition. It seems unlikely that any excess gas taken up from the flowing adsorbate would be nontitratable.

DISCUSSION

The uncertainty involved in comparing the pulse and conventional methods is difficult to assess. Real changes in hydrogen uptake from one pretreatment to the next are likely to frustrate the comparison at least as much as the accuracy of either measurement. Therefore, the excellent agreement of the present data with those of Wilson and Hall may be partly fortuitous. However, the basic similarity between the two sets of results must indicate that hydrogen adsorption on these samples was largely rapid

TABLE 3

OXYGEN CHEMISORPTION AND HYDROGEN-OXYGEN TITERS AT 25°C

Sample	Pretreatment	Hydrogen atoms[a] sorbed ($H_A \times 10^{-19}$)	Oxygen atoms[a] for titer ($O_T \times 10^{-19}$)	Hydrogen atoms[a] for titer ($H_T \times 10^{-19}$)	Oxygen atoms[a,b] sorbed ($O_A \times 10^{-19}$)	($H_A + 2O_A$) $\times 10^{-19}$	($O_A + 1/2H_A$) $\times 10^{-19}$
2.7% Pt[c] on SiO_2	Oven dried 120°C Reduced 1 hr 500°C	6.29	7.21	15.01	3.95	14.19	7.10
0.5% Pt[d] on SiO_2	Oven dried 120°C Reduced 1 hr 500°C	0.82	1.06	2.02	0.63	2.08	1.04
2.0% Pt[c] on SiO_2	Oven dried and Reduced 17 hr at 500°C	6.07	8.26	16.19	5.10	16.27	8.13

[a] Values are per gram of catalyst.

[b] Samples were rereduced to determine O_A experimentally.

[c] Prepared by chemideposition (*23*).

[d] Prepared by impregnation with chloroplatinic acid.

and irreversible at 25°C. On this basis, the stoichiometry of hydrogen chemisorption on platinum derived from static measurements may also be applied to the flow data, and indeed when hydrogen uptakes were related (*1–3*) to mean crystallite size in this way, the experimental data reflected platinum dispersion moderately well ($0.2 \leq H/Pt \leq 1$).

This was by no means certain. Germain *et al.* (*20*), for example, studied oxygen chemisorption and hydrogen–oxygen titrations on platinum–alumina by a gravimetric method, and hence were able to measure hydrogen uptakes both in the presence of hydrogen and after evacuating the ambient gas for 40 min. They concluded that some 50% of the hydrogen adsorbed at 20°C and 200 Torr was removed by this evacuation, and therefore reversibly adsorbed on the platinum. Clearly, the present correspondence between static and flow data would not be found if 50% of the hydrogen included in the conventional measurement was reversibly adsorbed. However, the values obtained by the static volumetric method are significantly less than the total uptake at 200 Torr, since the positively sloping isotherm is normally extrapolated to zero pressure (*3*). In addition, distinctions between reversible and irreversible adsorption are necessarily made by experiment and the pulse technique is particularly empirical in this respect. In one experiment, for example, a platinum–silica catalyst, left one hour in flowing nitrogen after the measurement of hydrogen adsorption, took up a further 11% of the original hydrogen monolayer; a quantity which would undoubtedly correspond to reversible adsorption in the experiments of Germain *et al.* (*20*).

These differences help reconcile the observations of Germain *et al.* (*20*) with our own. However, it is also possible that the relative volumes of reversibly and irreversibly adsorbed gas may vary from one catalyst to another. Although the two are not directly comparable, Cormack and Moss (*21*) found that from 3–50% of the carbon monoxide sorbed on platinum at 25°C and 1 Torr was readily desorbed, depending on dispersion. Such differences would cause disparity between the uptakes measured by the pulse and static methods and therefore correspondence with static data may not be completely general. However, the low hydrogen uptake on 0.5% platinum–alumina is the only possible example of such an effect uncovered in the present work.

Hydrogen chemisorption at elevated temperatures was not subject to the same treatment. In keeping with studies of hydrogen desorption from platinum (*9*, *22*), the volume of strongly bound gas decreased with temperature while reversible sorption increased. Therefore, the data obtained cannot be interpreted on the same basis as those obtained by the static procedure.

The pulse method was sufficiently versatile to measure oxygen chemisorption and the titration of adsorbed oxygen with hydrogen. These data were also only slightly different from those obtained conventionally and may be used to provide a number of internal checks on the validity of the flow technique.

The titration of adsorbed oxygen with hydrogen has been suggested as a means to measure platinum dispersion (*18*, *19*), providing a magnification ($2x + y/y$ in Eq. i) relative to hydrogen adsorption alone. However, the procedure has general utility only if the relationship between x and y is constant. Wilson and Hall (*3*) showed that it was not.

Titers were originally suggested (*18*) to minimize blank corrections in the static method, which become increasingly important as metal area decreases. No blank was ever observed using the pulse method and in principle, therefore, it should be possible to measure small metal areas accurately. Without question, however, the real merit of the pulse method is its simplicity. The necessary equipment is readily fabricated and inexpensive. The measurements are made rapidly, no unusual skill is required, and the operations lend themselves to automation. More marginal advantages over the static method include simpler maintenance over an extended period and the fact that pretreatment is facilitated by the flow mode of operation (high-vacuum apparatus and reduction in flowing hydrogen are relatively incompatible by comparison).

CONCLUSIONS

The pulse technique provides a simple way of measuring fast, irreversible chemisorption. For the catalysts examined, this quantity corresponded well to conventional data for hydrogen adsorption on platinum at 25°C and gave a reliable estimate of platinum dispersion using a model derived from the static measurements. Hydrogen uptakes at elevated temperatures require more careful interpretation.

It seems probable that the method would yield similarly useful results for the other catalytic metals of group VIII of the periodic table, since the clean metals adsorb hydrogen rapidly and with an appreciable binding energy. However, the two types of measurement are fundamentally different and the wealth of conventional data in the literature cannot be applied against the flow measurements as a matter of course.

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