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On the Use of the Dynamic Pulse Method to Measure Metal Surface Areas

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The use of the dynamic pulse method to measure supported Pt metal surface areas has been studied. In particular, variables such as injected pulse volume, eluted pulse area measurements, effect of carrier gas, and the pulse–volume to catalyst surface area ratio were considered. The volume of the injected pulse relative to the dead space of the reactor was found to be critical. When the volume of the injected pulse was too large, a nonlinear thermal conductivity detector response resulted. This nonlinearity was particularly evident when H_2 was used as an adsorbate in a He carrier gas. Due to slow reversible H_2 adsorption, eluted H_2 peaks were noticeably asymmetric. Because of extensive tailing, peak area measurements were found to be unreliable. A new method to estimate metal surface areas based solely on either eluted H_2 or CO peak heights is described. The fraction of H_2 and CO reversibly adsorbed was determined from the peak heights of the eluted pulse. Thirteen percent of the H_2 and 4.4% of the adsorbed CO were found to be reversibly adsorbed.

INTRODUCTION

The use of the dynamic pulse method to measure the metal surface areas of working catalysts is used in a large number of surface chemistry laboratories. The technique was pioneered by Grüber (*1*) and Roca *et al.* (*2*). It has been described in detail by Freel (*3*). In this method measured volumes of an adsorbate gas are pulsed over a catalyst until successive peak heights, as measured by gas chromatography, are of equal height or integrated peak areas are constant. The total gas uptake may easily be obtained by taking the difference between the areas of the eluted and injected pulses. Because surface area measurements obtained using the pulse method do not, in general, include reversible adsorption, a comparison between results obtained using this method and those determined using standard static adsorption measurements must be made cautiously. In spite of this limitation, the dynamic pulse method is still the most versatile and most widely used technique to measure supported metal surface areas. Unfortunately, experimental variables such as: relative pulse volume, contact time, eluted pulse area measurement, carrier gas used, and the catalyst weight to injected pulse volume ratio are subject to rather wide variations from one laboratory to the next. Because changes in these variables can result in large differences in surface area measurements, there is a need to standardize such measurements in order to ensure more meaningful comparisons between catalytic results obtained in different laboratories.

The purpose of this research is to examine these variables more critically and provide warnings concerning operating conditions which might lead to substandard surface area determinations.

EXPERIMENTAL METHODS

Flow system. A flow system which enables use of the reactor as either a pulse microreactor or a single pass reactor has been constructed and is described in detail elsewhere (*4*). Basically, it consists of two 6-

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port valves and a 4-port valve manufactured by the Valco Instruments Co. They were zero volume fitting valves and were equipped with ceramic-filled Teflon seals. Interconnecting lines were assembled using stainless-steel tubing of standard commercially available sizes; generally, 3.175, 1.587, or 6.35 mm o.d. for connections between gas cylinders and the 3 tube mixer (Matheson Corp.). All connections were made using standard size commercially available stainless-steel swagelock fittings. The gas chromatograph (Perkin-Elmer model Sigma-3B, equipped with a thermal conductivity detector and numerical readout flow controllers) was located downstream of the reactor. A stainless-steel column 1 m in length and having an outside diameter of 3.175 mm packed with Carbosive S (100–120 mesh) was used.

The microreactor was constructed from Pyrex tubing (o.d. = 12 mm) and had a total volume of 4.4 ml. It had a length of 70 mm and was connected to the flow system using 3.1-mm tubing and swagelock fittings. The catalyst was held in place by means of a fritted disk and quartz wool. The Pyrex microreactor could be replaced by an infrared cell also capable of operating either as a pulse microreactor or a single pass differential reactor, thus adding further versatility to the flow system.

Materials. The gases used in this study were subjected to the following purification treatment: CO (New England Oxygen research grade) was purified by passing it through a molecular sieve. H_2 (New England Oxygen research grade) was purified by first passing it through a Deoxo unit to convert O_2 impurities to H_2O, which was then removed by a molecular sieve maintained at 77°K by means of a liquid N_2 trap. He and N_2 (New England Oxygen high purity) were passed through an oxygen trap (Model OT-1, Separations Co.) backed by a molecular sieve maintained at 77°K by means of a liquid N_2 trap. Because results obtained using the dynamic pulse technique are extremely sensitive to trace amounts of H_2O and O_2 in the carrier gas stream, care was taken to exclude these contaminants from the catalyst sample. The oxygen concentration in the carrier gas at the sample was measured and found to be about 0.1 ppm. H_2O levels were much lower.

The silica or alumina-supported Pt samples used in this study were prepared by impregnation. Initially, the appropriate weight of $H_2PtCl_6 \cdot 6H_2O$ was dissolved in an amount of deionized water sufficient to ensure the complete wetting of the support. This solution was mixed with either Cab-O-Sil, Grade M-5 or Alon-c (Cabot Corp., Boston, Mass.) until a slurry having the consistency of a thin paste was formed. The slurry was then dried in a vacuum desiccator at room temperature for 1 or 2 days and stirred regularly during the drying process to retain uniformity. The dried catalyst was pressed into thin disks and ground into a fine powder before use.

Procedure. A fresh supported Pt catalyst was treated as follows: heated in flowing He (30 ml/min) as the temperature was increased from 25 to 130°C at a rate of 10°C/min, gas stream switched to H_2 (30 ml/min), and temperature increased from 130 to 380°C at a rate of 10°C/min, reduced in flowing H_2 for 1 hr at 380°C, treated in flowing He (30 ml/min) for 10 min, and temperature reduced from 380 to 25°C in flowing He at 10°C/min.

Prior to a chemisorption measurement, the sample was treated as follows: heated in flowing O_2 (30 ml/min) as the temperature was increased from 25 to 250°C at a rate of 10°C/min, treated in flowing O_2 at 250°C for 30 min, gas stream switched to flowing He at 250°C for 10 min followed by reduction in flowing H_2 (30 ml/min) at 250°C for 1 hr, treated in flowing He at 250°C for 30 min followed by cooling in flowing He to 25°C. When this procedure was used, high metal dispersions were obtained. In some cases, lower Pt dispersions were obtained by modifying the initial pretreatment of a fresh catalyst sample, as follows: heated in flowing H_2 (30 ml/min) as the temperature was increased from 25 to 300°C (380°C in the case of the $Pt-Al_2O_3$ samples) at a rate of 10°C/min, reduced in flowing H_2 for 1 hr at either 300 or 380°C, treated in flowing He (30 ml/min) for 30 min, and temperature reduced in flowing He as previously described. This procedure inhibits the dissolution of H_2PtCl_6 in its waters of hydration and, therefore, prevents extensive spreading over the support. The H_2PtCl_6 is essentially reduced prior to surface migration, resulting in the formation of relatively large crystallites with lower metal dispersions (5).

Chemisorption measurements were made by injecting 100 μl pulses of adsorbate gas (H_2 or CO) through the catalyst sample at 25°C. The volume of gas adsorbed was obtained by measuring the difference in the areas of the eluted and injected pulses. To test the linearity of the thermal conductivity detector response as a function of adsorbate gas concentration, provisions were made to replace the 100 μl injector by one having a volume of either 200 or 550 μl.

When N_2 was used in place of He as the carrier gas, pretreatment was carried out using the same procedure as described above. The He carrier gas stream was replaced by N_2 after the pretreatment was complete and the catalyst had been cooled to room temperature. The carrier gas flow rate used in the chemisorption experiments was 30 ml/min.

RESULTS

The Effect of Reactor Volume

To study the effect of reactor volume on the linearity of the thermal conductivity detector response, the dead space volume (empty reactor pulse associated tubing) was varied, as shown in Fig. 1. By short circuiting the reactor, the dead space could be reduced to a very small volume (Figs. 1 B and C). When this was done, the thermal conductivity response was nonlinear, as shown by the difference in the integrated areas of the peaks. Additionally, when the dead space volume was very small, pulse splitting occurred when He was used as the carrier gas. This effect was completely eliminated when N_2 was used instead of He. This effect is due to the relatively small difference in thermal conductivity between He and H_2 and the much larger difference in thermal conductivity between N_2 and H_2. Because of these results, care should be taken to ensure that the reactor volume is such that a linear thermal conductivity response is obtained. This effect becomes more important when He is used as a carrier gas to measure H_2 chemisorption by the dynamic pulse method. In the present study, a reactor having a volume of 4.4 ml appeared to be adequate for an injected pulse having a volume of 200 μl. However, better results were obtained using a 100 μl pulse.

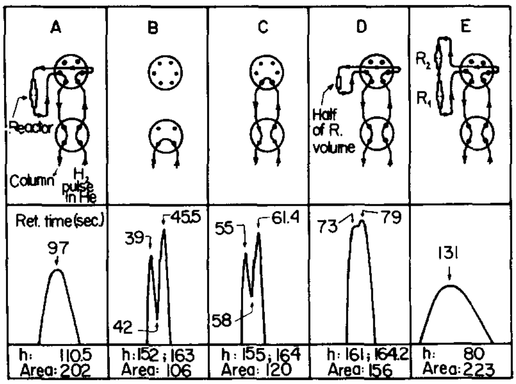


FIG. 1. The effect of dead space volume on detector response.

The effect of the injected pulse volume on the linearity of the thermal conductivity detector response using He as a carrier gas was studied by changing both the pulse volume and the concentration of adsorbate gas in the injected pulse. The connections shown in Fig. 1A were used in this study. The results are shown in Fig. 2. For the 100 μl pulse, a linear relationship between peak height and adsorbate gas concentration was obtained for both CO and H_2. Because peak height is proportional to adsorbate concentration, it can be concluded that the injection of a 100 μl pulse results in a linear ther-

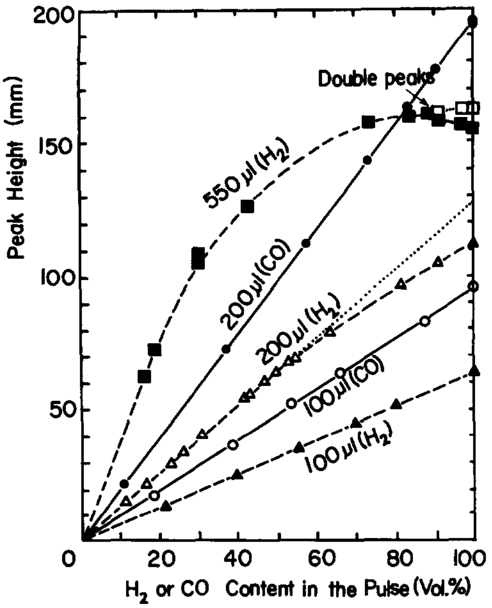


FIG. 2. The effect of injected pulse volume on the linearity of the thermal conductivity detector response. Peak height vs concentration of H_2 or CO in pulse. Connections are in the A position (see Fig. 1).

mal conductivity response. When the volume of the injected pulse was increased to 200 µl, a linear relationship between peak height and CO concentration was obtained. However, for H_2 small deviations from linearity were observed for H_2 gas concentrations in excess of 55%. The nonlinearity between peak height and H_2 concentration was very large when the volume of the injected pulse was increased to 550 µl. Split peaks occurred when the concentration of H_2 in the injected pulse exceeded 90%. The greater linearity observed for injected CO pulses is due to the much larger difference in thermal conductivity between the adsorbate and the carrier gas, in this case, He.

Thermal conductivity detectors give a linear response only at relatively low concentrations of the sample gas. As the concentration of the sample in the carrier gas is increased, the thermal conductivity response becomes increasingly more nonlinear. In the case of H_2 in a He carrier gas, this nonlinearity is more pronounced due to a change in the sign of the thermal conductivity detector response at high H_2 concentrations (*6*). Under these conditions, double peaks result.

The volume of the injected pulse relative to that of a monolayer has been discussed as an arbitrary variable in the literature. Freel (*3*) concluded that good results were obtained when the volume of the injected pulse was about a quarter of that corresponding to a monolayer. Wanke *et al.* (*7*), on the other hand, found that the volume corresponding to a chemisorbed monolayer was strongly dependent on the volume of the injected pulse. The results of this study strongly suggest that when He is used as a carrier gas, incorrect results will be obtained using H_2, due to the nonlinearity of the response of the thermal conductivity detector when the injected pulse is too large. Because these results were obtained without a catalyst we are of the opinion that these discrepancies are experimental in nature. Good results can be obtained using H_2 in a He carrier gas stream, provided that the volume of the injected pulse relative to the volume of dead space (sample loop through the detector including the reactor) is small. When H_2 is used as an adsorbate gas, N_2 is a better choice as a carrier gas than He. The use of N_2 as a carrier gas, however, introduces other problems. Many group VIII metals, notably Fe and Ru, chemisorb N_2 at pretreatment temperatures and in addition, form nitrides. The only other acceptable choice is pure Ar. However, Ar is rather expensive for large scale use. For this reason, the use of He as a carrier gas is attractive provided care is taken to ensure the linearity of the thermal conductivity response when H_2 is used as the adsorbate gas. The volume of the injected pulse is not as critical for CO in a He carrier gas.

In the presence of an adsorbent, the eluted H_2 pulse is broadened due to the presence of a reversibly adsorbed phase. This broadened pulse becomes very difficult to integrate because of its asymmetry and extensive tailing. Because the asymmetry of the eluted pulse depends upon the extent of the reversibly adsorbed phase, the possibility of determining the metal surface area solely from the peak height of the eluted pulse is attractive. To explore the existence of such a relationship the eluted peak height at monolayer coverage was obtained as a function of relative catalyst weight ($m_r = (m_0 - m)/m_0$) where m_0 was the largest weight of catalyst charged to the microreactor during the study and m was the weight of catalyst removed in order to reduce the total metal surface area. In this study, the effect of both injected pulse volume and reactor dead space volume was considered for a 6% Pt–Al_2O_3 catalyst having a metal disperson of 54%. The results are shown in Fig. 3. For an injected pulse of 100 μl, a linear relationship between the H_2 eluted peak height and the relative amount of catalyst m_r was obtained with the reactor connections in either the A or E position of Fig. 1. When the volume of the injected pulse was increased to 200 μl, the relationship was linear in the E position but slightly nonlinear in the A position. The nonlinearity observed for the 200 μl pulse was predictable in view of the results shown in Fig. 2, i.e., when the concentration of H_2 in the He pulse was increased, a nonlinear thermal conductivity detector response was observed. The results using CO as an adsorbate gas in a He carrier gas are shown in Fig. 4. The relationship between eluted peak height and the relative amount of catalyst used was linear and did not depend on the volume of the injected phase. Because of these results, we conclude that surface areas can be determined solely from eluted peak heights using either H_2 or CO as an adsorbate in a He carrier gas. When H_2 was

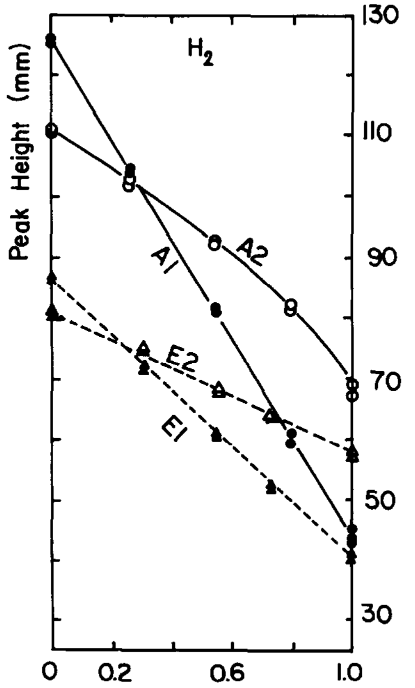


FIG. 3. Eluted peak height of H_2 pulses at monolayer coverage as a function of relative catalyst weight, m_r. A_1, 100 μl pulse; A_2, 200 μl pulse; E_1, 100 μl pulse; E_2, 200 μl pulse. Connections are either in the A or E position (see Fig. 1) and m_0 = 0.227 g.

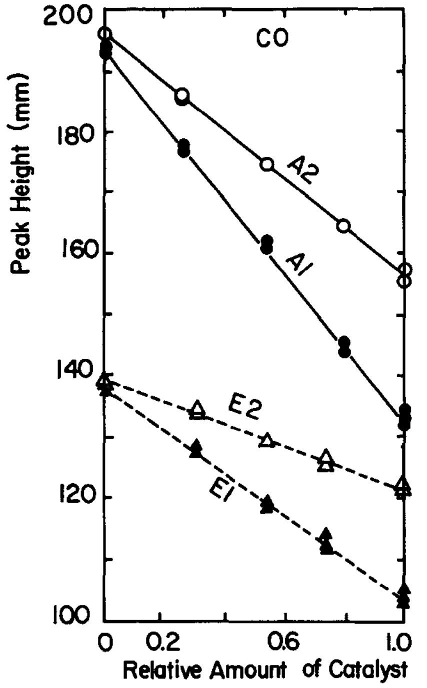


FIG. 4. Eluted peak height of CO pulses at monolayer coverage as a function of relative catalyst weight, m_r. A_1, 100 μl pulse; A_2, 200 μl pulse; E_1, 100 μl pulse; E_1, 200 μl pulse. Connections are either in the A or E position (see Fig. 1) and m_0 = 0.227 g.

used, better results were obtained when the volume of the injected pulse was small. Blank measurements using silica or alumina showed no decrease in the eluted peak height with the relative amount of catalyst used. Additionally there was no uptake of H_2 or CO by the support under the conditions used in the dynamic pulse method.

The implications of these results are not only important to users of the dynamic pulse method, but can also be used to estimate surface areas and consequently metal dispersions both rapidly and accurately. This can be accomplished by means of a simple calibration.

A plot of H_2 eluted peak height as a function of Pt metal surface area is shown in Fig. 5 for two catalysts having different dispersions. A 100 μl H_2 pulse was used in this study and the surface area was changed by varying the amount of catalyst charged to the reactor. Surface areas were accurately measured for each catalyst so that the total Pt surface area could be determined from the weight of the catalyst charged to the reactor. The results, shown in Fig. 5, show an excellent linear relationship between eluted H_2 peak height and metal surface area regardless of Pt dispersion or support used. Integrated peak areas corresponding to the eluted H_2 pulse were independent of the total surface area. However, as the surface area became large, reversible adsorption caused considerable distortion and tailing of the eluted peak. Because of this, integration of the resulting eluted peaks becomes difficult. The eluted peaks are shown in Fig. 6 as a function of Pt metal surface area. Small shifts in the baseline coupled with very long elution times (in excess of 15 min) can cause a substantial error in the eluted peak area. The data are summarized in Table 1.

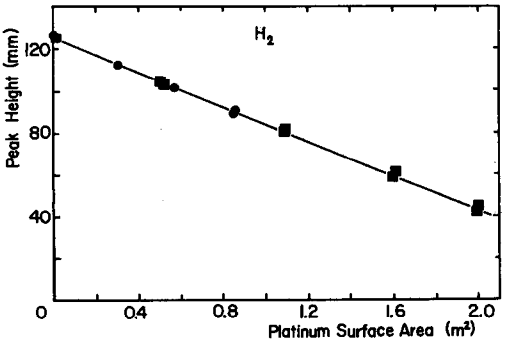


FIG. 5. Eluted H_2 peak height as a function of Pt surface area. Peak heights were measured following the addition of a 100 μl H_2 pulse to a catalyst previously saturated with H_2. Six percent Pt-SiO_2, dispersion = 19.5%; 6% Pt-Al_2O_3, dispersion = 54%.

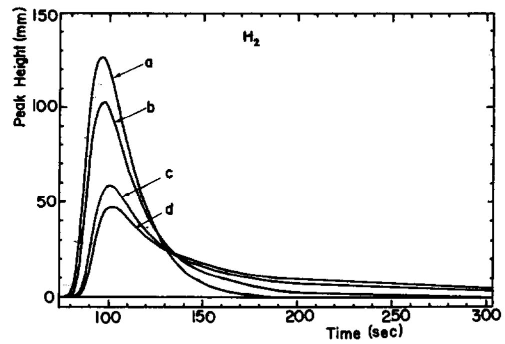


FIG. 6. Eluted H_2 peak heights as a function of relative catalyst weight. a, $m_r = 0$; b, $m_r = 0.257$; c, $m_r = 0.795$; d, $m_r = 1$. Connections are in the A position (see Fig. 1) and $m_0 = 226.8$ g.

In determining Pt surface areas by the eluted peak height method described above, care must be taken to ensure that any reversibly adsorbed H_2 remaining on the catalyst has desorbed prior to the addition of the incoming H_2 pulse. We have found that best results were obtained when the interval between incoming H_2 pulses was about 15 mins. If the H_2 pulse is added too soon, the height of the eluted H_2 peak will be too large and the surface area will be slightly overestimated.

The Effect of CO Surface Coverage on Eluted H_2 Peak Heights

Because chemisorbed hydrogen is readily displaced from Pt by CO, it is of interest to consider the extent to which chemisorbed CO blocks the slow reversible adsorption of H_2. If the suppression of slow reversible H_2 adsorption on surface sites covered by CO

TABLE 1

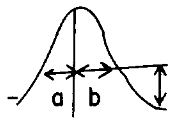
Eluted Pulse Characteristics Obtained by Injecting 100 μl Pulse through a 6% $Pt\text{-}Al_2O_3$[a] Catalyst at Monolayer Coverage

Relative catalyst weight m_r[b]	Retention time (sec)	Peak asymmetry[c]		Half width (sec)	Peak height (mm)	Relative integr. area	
		At 50%	At 10%			300 sec	900 sec
0	97.2	1.92	3.25	27.7	126	1.00	1.00
0.257	98.5	2.11	4.63	30.5	104	1.00	1.01
0.539	100	2.21	6.25	31.2	81	0.99	1.00
0.795	102.3	2.52	8.16	34.5	59	0.96	1.00
1.0	104	2.72	8.88	38.8	43	0.89	0.99

[a] Dispersion = 54%, S = 8.9 m^2 Pt/g.

[b] $m_r = (m_0 - m)/m_0$; $m_0 = 226.8$ mg.

[c] Peak asymmetry = b/a



is complete, a linear relationship between eluted H_2 peak height and the fraction of the surface covered by CO should result. The results of this experiment for three different catalysts are shown in Fig. 7. Because linear relationships were obtained for all three catalysts, we must conclude that CO completely blocks surface sites on which slow reversible H_2 adsorption occurs.

The fact that Pt surface sites which are blocked by CO completely suppress reversible H_2 adsorption suggests that a linear relationship between eluted H_2 peak height and the surface area not covered by adsorbed CO should be obtained. In other words, the extent of reversibly adsorbed hydrogen should depend solely on the surface area covered by hydrogen atoms. The results of this experiment are shown in Fig. 8. Data points corresponding to all three catalysts studied fall on the same line, showing that this relationship is independent of Pt dispersion and support.

The result of the relationships shown in Figs. 5–8 suggests a quick and easy way to determine supported Pt metal surface areas. Following reduction of the catalyst in

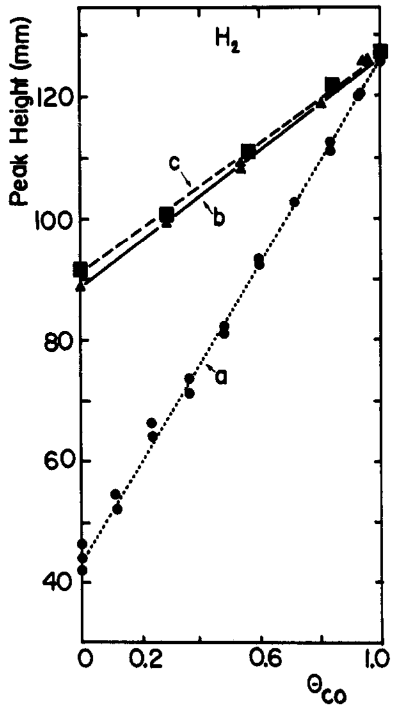


FIG. 7. H eluted peak height as a function of CO surface coverage. ●, 6% $Pt\text{-}Al_2O_3$, dispersion = 54%; ▲, 6% $Pt\text{-}Al_2O_3$, dispersion = 12%; ■, 6% $Pt\text{-}SiO_2$, dispersion = 19.5%.

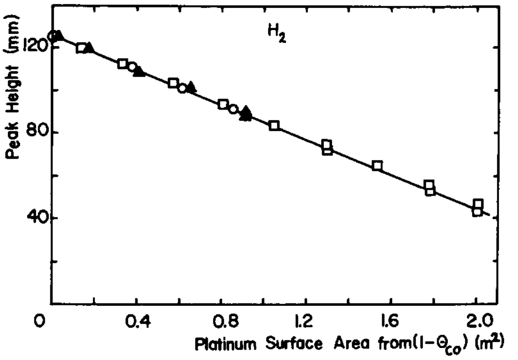


FIG. 8. H_2 eluted peak height as a function of the surface not covered by CO. □, 6% $Pt-Al_2O_3$, dispersion = 54%; ▲, 6% $Pt-Al_2O_3$, dispersion = 12%; ○, 6% $Pt-SiO_2$, dispersion = 19.5%.

flowing H_2, an accurately measured volume of H_2 is pulsed over the catalyst. From a calibrated plot such as that shown in Fig. 5 the total Pt surface area can be determined. When this measurement is coupled with the total weight of the catalyst, the dispersion can be calculated. This procedure does not require the desorption of chemisorbed hydrogen followed by subsequent hydrogen chemisorption measurements.

Finally, it is possible to estimate the amount of reversibly adsorbed H_2 and CO from plots such as those shown in Figs. 4 and 5. Chemisorption measurements on 226.8 mg of a reduced 6% $Pt-Al_2O_3$ catalyst yielded 443.7 μl of irreversibly adsorbed H_2 and 665.8 μl of chemisorbed CO. Because the peak heights shown in Figs. 4 and 5 can be related to the amount of reversibly adsorbed H_2 and CO, respectively, extrapolation of these lines to zero peak height yields the total Pt surface area which is required to completely adsorb a 100 μl pulse reversibly. In the case of H_2, this extrapolation gives a value 3.04 m^2 Pt. This 3.04 m^2 Pt would adsorb 674.4 μl of H_2 irreversibly. The fraction of H_2 reversibly adsorbed is, therefore: reversible/total = 100/(100 + 674.4) = 0.13. Using a similar procedure, the fraction of reversibly adsorbed CO is found to be 0.044, a value considerably lower than that found for H_2 as expected.

It has often been stated that the dynamic pulse technique cannot be used to measure weakly bound H_2 or CO and therefore comparisons between the dynamic pulse method and the static method should be made with care. We have shown, however, that it is possible to obtain reasonable estimates regarding the fraction of the adsorbed phase which is reversibly adsorbed.

CONCLUSIONS

The following conclusions and recommendations emerge from this study:

(1) When the dynamic pulse method is used to measure metal surface areas the volume of the injected pulse, relative to that of the reactor, including dead space, cannot be taken arbitrarily. It is advisable to adjust the volume of the injected pulse in the absence of an adsorbent to ensure a linear response from the thermal conductivity detector.

(2) When hydrogen is used as an adsorbate, the choice of a carrier gas should be made with care. He can be used as a carrier gas provided consideration is given to the recommendations in (1). The use of N_2 as a carrier gas will in general be more satisfactory than He when H_2 is used as the adsorbate. When CO is used as an adsorbate, He is a good choice as a carrier gas.

(3) The asymmetry and extensive peak tailing of eluted chromatographic peaks which result as a consequence of the slow reversible H_2 adsorption, may lead to errors when peak areas alone are considered. Because of the linear relationship obtained between peak heights and metal surface area covered by hydrogen, we recommend that this method be used in the estimation of metal surface areas. The practice of simply taking the difference in peak height between eluted pulses at monolayer coverage and

eluted pulses which have been partially adsorbed by the catalyst will, in general, result in gross errors.

(4) It is possible to estimate the fraction of reversibly adsorbed H_2 and CO using the linear correlations between peak height and surface area described in this investigation.

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