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Gas Chromatographic Study of Hydrogen Adsorption on Supported Metals

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A method of obtaining chemisorption isotherms from gas chromatographic data is described. It is shown that by the combination of a slug technique with analysis of retention times, adsorption can be studied even for systems which are not fully reversible. Results obtained with platinum, rhodium, and palladium on alumina carriers are reported and their interpretation in terms of metal dispersion is discussed in comparison with results derived from other techniques.

INTRODUCTION

Chemisorption methods have become the most useful single tool for the measurement of specific metal area or metal dispersion in supported metal catalysts. In particular, the chemisorption of hydrogen as determined by static, volumetric techniques (*1–3*) and the chemisorption of carbon monoxide as measured by flow techniques (*4, 5*) were described in detail and were widely used in the course of several studies of supported metal catalysts (*6–9*). More recently, a hydrogen–oxygen surface titration technique was developed (*10*), based on a volumetric determination of the amount of hydrogen consumed by reaction with a chemisorbed oxygen layer and subsequent chemisorption on the metal. The titration method was also carried out in a flow system (*11, 12*). While adsorption data obtained with hydrogen are more easily interpreted in terms of surface area than are carbon monoxide data, the CO flow techniques are much simpler experimentally.

In the study reported here, we attempted to combine the advantages of both approaches by determining hydrogen isotherms from gas chromatographic retention time measurements, that is by analysis of the shape of elution peaks. The objective was to demonstrate generally the applicability of adsorption isotherm determinations from gas chromatographic retention times to other than pure physisorption systems, and to evaluate the experimental parameters for several supported platinum metals.

PROCEDURE

Adsorption isotherms can be obtained from gas chromatographic measurements by either frontal analysis or peak elution. In principle, frontal analysis is applicable to chemisorption without difficulties and the method was first successfully used for metal area determination by Hughes *et al.* (*4*). The elution techniques (measurement of retention time of a sample slug as a function of concentration) as first demonstrated by Cremer *et al.* (*13*) for physisorption systems, requires "ideal" gas chromatographic conditions, that is very fast equilibration and freedom from diffusional effects. Although the application of the elution technique to chemisorption is therefore somewhat limited, the technique is made particularly attractive in comparison with static methods or frontal analysis on account of three aspects:

1. Clean experimental conditions with very low residual gas concentrations (com-

parable to UHV conditions) can be easily obtained.

2. Due to the very short contact times involved, problems of decomposition of reactive gases or vapors are minimized, an aspect which was utilized extensively by Eberly *et al.* (*14*) in studies of hydrocarbon adsorption at high temperatures.

3. The elution technique is sensitive only to processes occurring at a rather fast rate. As will be shown in detail later, slow activated adsorption on typical catalyst carriers does not effect the retention times and thus support corrections are not required.

The major difficulty in the application of the elution technique to chemisorption systems lies in the lack of reversibility. The term "reversible" as used here simply means that the rate of desorption at a given temperature is fast enough so that complete desorption will occur within a time comparable to the experimental time parameters involved, e.g., several minutes for typical elution measurements. Previous experience from static work with the hydrogen/platinum system (*2*) as well as preliminary measurements with the elution technique (*15*) showed that hydrogen adsorption on our catalysts was not completely reversible in the temperature range 25–500°C. The amounts of hydrogen eluted in 15 min were always less than the amount injected.

Therefore frontal analysis in the form of pulse elution was combined with the slug difference technique described earlier (*5*). A pulse of hydrogen of known volume is injected in front of the catalyst bed and the shape and area of the eluted pulse are recorded. The difference in area of the two pulses gives the amount of gas which is "irreversibly" adsorbed. It serves as the base point for the isotherm obtained from frontal analysis of the eluted pulse. Thus the method yields not only the total adsorption corresponding to the maximum pressure in the pulse, but also the shape of the isotherm up to this pressure and the amount of gas irreversibly adsorbed. In addition to information on total metal area one obtains some information on the surface energy spectrum involved.

EXPERIMENTAL

Apparatus

A schematic diagram of the apparatus used is shown in Fig. 1. The carrier gas was introduced through a capillary with a pressure drop large compared to that of the rest of the system. A wide range of flow rates was investigated and rates 15–70 cc/min were found satisfactory. The results reported here were obtained with carrier gas flow rates of 35 cc/min. With retention times in the order of 1 min, constancy of flow rates and their exact determination is of extreme importance. The hydrogen samples were injected downstream of the capillary and the reference cell, giving improved flow stability. A somewhat different procedure was followed in the initial experiments (*15*), but the scheme shown in Fig. 1 proved superior in reproducibility. A thermal conductivity cell served as detector. The response for hydrogen was linear up to a pressure of about 80 Torr. Column length was 40 cm with all samples. The internal column diameter was 0.3–0.5 cm, depending on sample size. Sample sizes of 2–7 g were used. The column was thermostated to ±0.5°C and the samples could be reduced *in situ*. A reference column filled with glass beads provided a sample bypass with dead space and diffusional characteristics similar to those of the packed column. Thus breakthrough times and peak profiles of a nonadsorbable gas were identical over both paths. The bypass was used in the determination of hydrogen pulse sizes and in the thermal desorption experiments.

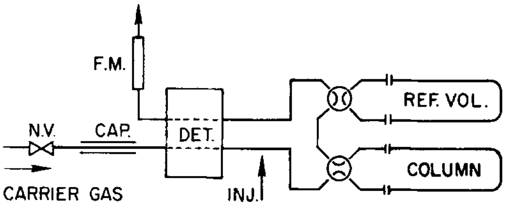

FIG. 1. Schematic diagram of flow apparatus.

Materials

The carrier gas (nitrogen or helium) was purified by passing it over a copper catalyst, followed by a drier and by cold traps. The catalysts used were a 0.5% platinum on eta-alumina (210 m^2/g BET area) as described earlier (*2*), as well as three experimental catalysts,* containing 2% platinum, palladium or rhodium on γ-alumina of 60 m^2/g BET area. All catalysts were used in the form of crushed pellets with particle sizes in the range of 1 to 2 mm.

Pretreatment

After air calcination all samples were reduced in flowing hydrogen for 16 hr at 500°C and then exposed to atmosphere at room temperature. Before each adsorption run the samples were reduced *in situ* for two hours at 500°C in a hydrogen flow of 50 cc/min, then purged at this temperature for 16 hr in the carrier gas (flow rate of 35 cc/min) and finally cooled in the carrier gas stream to the desired temperature of adsorption. In several cases purge times were substantially extended in order to check the possibility of partial reoxidation of the metal during these long pretreatments. Up to 72 hr of purge there was no effect on the subsequent hydrogen uptake. Thus the pretreatment procedure chosen insures complete desorption of the hydrogen which is present from the reduction step, but at the same time avoids any measurable reoxidation of the metal component.

CALCULATION OF ISOTHERMS

The calculation of adsorption isotherms from gas-chromatographic data was demonstrated in detail by Gregg and Stock (*16*), who evaluated the shape of gas-solid chromatograms obtained by frontal analysis, and who could show good agreement between the calculated isotherms and the ones measured directly by a standard gravimetric technique. Cremer and Huber (*13*) calculated isotherms from the shape of single elution peaks, using a simple procedure for the correction of diffusional effects described by Huber (*17*) and by Bechtold (*18*). Further verifications of these methods as presented by several authors were reviewed by Habgood (*19*).

The basic relationship between the adsorption isotherm and the gas-chromatographic parameters is given by

$$\frac{dx}{dc} = V_g, \qquad (1)$$

where x is the amount adsorbed in moles per gram, c the concentration of adsorbate in the carrier gas in moles per cc, and V_g is the specific retention volume defined by

$$V_g = \frac{t_r \cdot F}{m}. \qquad (2)$$

Here t_r is the net retention time $(t - t_0)$, F the volume flow rate, and m the mass of adsorbens. By integration of Eq. (1)

$$x = \int_0^c V_g dc, \qquad (3)$$

thus the amount adsorbed can be directly calculated if the retention volume V_g is known as a function of concentration or pressure. This is exactly the information contained in the elution profile.

The evaluation of the data presented here was carried out after converting Eq. (3) by substitution of Eq. (2) to

$$v_a = \frac{C}{m} \cdot \int_0^h t_r dh \qquad (4)$$

Here the amount adsorbed v_a is expressed in cc (STP)/g and the concentration c is replaced by the height of the detector signal h. A linear detector response was verified over the full experimental pressure range. Equation (4) was evaluated by graphical integration as shown in Fig. 2 for an ideal peak DFH. Thus the area ACFH gives the amount adsorbed at maximum pressure $p_{\max}$, while adsorption at any pressure lower than $p_{\max}$ is determined by integration to a correspondingly lower pressure, e.g., from the area ABGH for pressure p_1. The constant C in Eq. (4) was determined experimentally by integration of

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* These catalysts were kindly provided by Dr. H. Kral of W. C. Heraeus GmbH, Germany.

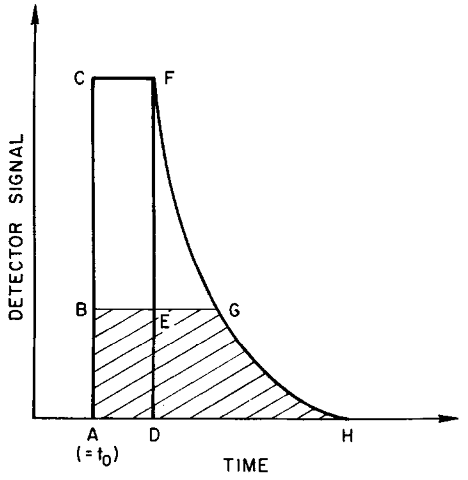

FIG. 2. Graphical integration of the retention time vs concentration curve (trailing edge FGH).

the area of a peak obtained upon injection of a known amount of sample.

Since diffusional broadening of the peaks or fronts is not accounted for in Eqs. (3) or (4), a correction for diffusion has to be applied to the peak shape before these equations can be used. We have chosen the method described by Bechtold (*18*), in which the distance (time) between leading edge and peak maximum is subtracted from the distance between trailing edge and maximum over the full pressure range covered by the peak. This correction is valid for a type I isotherm (sharp front) and based on the assumption that band broadening effects observed at the sharp front of the peak are equal to those affecting the diffuse trailing edge and that the retention time of the peak maximum is not affected by diffusion.

The validity of these assumptions can be tested experimentally: Peak maxima of smaller peaks should coincide with the corrected trailing edge of larger peaks. Corresponding experiments were carried out in the hydrogen/platinum system by injecting a series of pulses of varying size, and the above assumptions proved to be correct within the experimental error of the measurements of retention times. In addition these experiments indicated that under the conditions chosen there are no spurious effects due to nonequilibration, final width of the injected pulses, or overloading of the sample. Also, due to the column dimensions, particle sizes and flow rates used, the pressure drop across the catalyst bed was practically zero, so that a pressure correction was not required in any of the measurements reported here.

RESULTS AND DISCUSSION

Irreversible Adsorption

The amount of gas adsorbed "irreversibly" (v_{irr}) was defined in a purely operational manner as the amount not eluted at the adsorption temperature within a time of 12.5 min. The experimental values of v_{irr} for 3 catalyst samples as a function of temperature are summarized in Table 1, Column 2. They were obtained by taking the difference between the area of the injected pulse and the eluted pulse, carrying out the integration over a period of 12.5 min. The total adsorption then is the sum of this irreversible part and the reversible adsorption calculated from the retention times. For this approach to be valid, equilibrium has to be established in the adsorption step and the irreversible part should be independent of p_{max} or the size of the injected pulse.

This was tested experimentally and in Fig. 3 the irreversible adsorption of hydrogen on the 2% Pt/Al_2O_3 sample is plotted as a function of pulse size. Between 60 and 250°C the curves show the behaviour expected from theory: As long as the injected pulse is smaller than the amount which can be adsorbed irreversibly, the pulse is completely retained and v_{irr} increases linearly with pulse size. When the pulse size becomes larger than the limiting value of v_{irr}, the irreversible adsorption is practically independent of pulse size as it should be. At the higher temperatures (370 and 510°C), there is a distinct transition region and a pressure independent v_{irr} is only reached with a roughly twofold excess of hydrogen. This resembles the results obtained previously with carbon monoxide on platinum at room temperature

TABLE 1
SUMMARY OF THERMAL DESORPTION EXPERIMENTS
(v in cc(STP)/g)

Catalyst and temperature	$v_{\mathrm{irr},T}$	$v_{\mathrm{irr},T} - v_{\mathrm{irr},510°\mathrm{C}}$	$v_{\mathrm{therm.des.}}$
Platinum			
510°C	0.20	0	—
250°C	0.32	0.12	0.10
150°C	0.40	0.20	0.19
60°C	0.48	0.28	0.28
Rhodium			
510°C	0.32	0	—
370°C	0.44	0.12	0.10
250°C	0.75	0.43	0.43
150°C	1.21	0.89	0.90
55°C	1.92	1.60	1.53
Palladium			
510°C	0.12	0	—
370°C	0.11	0	0.04
250°C	0.15	0.03	0.12
150°C	0.25	0.13	0.22
80°C	0.39	0.27	0.26

(*5*) and indicates that the adsorption equilibrium is established more slowly than at the lower temperatures. Also, the magnitude of v_{irr} at 510°C is much larger than that expected from extrapolation of the values at lower temperatures.

It is tempting to attribute these effects to the support material. Although appreciable hydrogen adsorption (e.g., 0.15 cc(STP)/g) on nonplatinized alumina at 500°C was found in earlier volumetric work (*2*), direct adsorption on the support must be excluded here, since elution measurements on the alumina blanc showed no evidence of either reversible or irreversible adsorption over the whole temperature range up to 510°C. This is not in contradiction to the static results because the elution technique cannot detect slow, activated processes such as the adsorption of molecular hydrogen on alumina. However, in view of the fact that migration of hydrogen from the platinum to the support may be quite fast at these high temperatures (*20, 21*), we assume that the relatively large amount of irreversible adsorption found at 510°C (possibly also at 370°C) is at least partly due to such a surface diffusion effect.

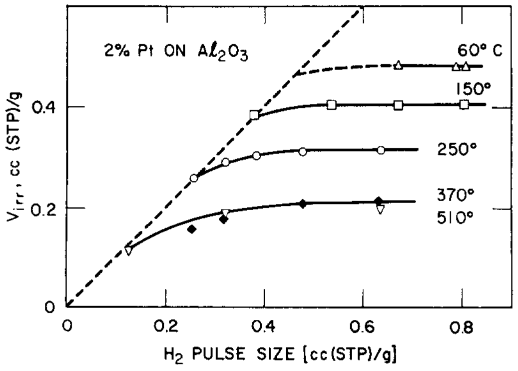

FIG. 3. Irreversible adsorption as function of pulse size.

Between 60° and 370°C the magnitude of v_{irr} decreases from about 0.5 to about 0.2 cc(STP)/g corresponding to a coverage of from $\theta \approx 0.6$ to $\theta \approx 0.25$. As we discussed before (*15*), this is to be expected on the basis of the heats of adsorption reported for this range of coverage (*22*). The fraction of hydrogen adsorbed irreversibly at 60°C also is in fair agreement with the value found gravimetrically by Boudart for platinum black at room temperature (*23*). The irreversible hydrogen adsorption on platinum at 200°C was recently utilized by Trambouze *et al.* (*24*), to determine metal dispersion by a modified slug flow technique.

Thermal Desorption

Further verification of the fact that the irreversible adsorption is strictly due to slow removal of hydrogen at low coverages and not due to a reaction of hydrogen with surface oxygen, was gained from thermal desorption experiments with the 2% Rh, Pd, and Pt on alumina catalysts. After an elution experiment was carried out at a given temperature T, the sample tube was cut off from the flow system using the bypass shown in Fig. 1. Then the temperature of the sample was raised to 510°C and the thermally desorbed hydrogen was determined by switching the sample tube back into the flow system. The results are summarized in Table 1, Column 4 in comparison with elution data. Column 2 gives v_{irr} measured by elution at the temperature T, Column 3 lists the calculated difference between $v_{\mathrm{irr},T}$ and $v_{\mathrm{irr},510^{\circ}}$ and Column 4 the amount of hydrogen thermally desorbed upon raising the catalyst temperature from T to 510°C. Except for palladium, where at least at the higher temperatures solution might be fast enough to interfere with the adsorption measurements, the agreement between Columns 3 and 4 is very good. With platinum and rhodium, v_{irr} can be desorbed quantitatively in any of the temperature intervals used.

It should be emphasized that on the basis of our experiments it cannot be decided whether the "irreversible" adsorption is due to nonequilibration caused by kinetic effects or due to very low equilibrium pressures at low coverages. Experimentally, we only see that as the coverage is decreased beyond a certain point, a further decrease in coverage proceeds at such a slow rate that it becomes practically unmeasurable. This could be caused by an increase in activation energy of desorption, which in this system can be taken as equal to the heat of adsorption and thus increases with decreasing coverage, or it could simply be due to the fact that the equilibrium pressure of the adsorbate decreases strongly with decreasing coverage as indicated by the shape of the isotherm. In the latter case, the equilibrium between the adsorbed layer and the hydrogen partial pressure in the carrier gas would be established and the slowness in desorption would be a mass transport phenomenon. Then of course a variation of the carrier gas flow rate will theoretically affect the fraction of adsorption, which by our definition, occurs irreversibly. Experimentally the flow rate was varied 15–70 cc/min and no such effect was found. However, this result is not conclusive because the magnitude of the effect within this range of flow rates could not exceed the overall experimental error.

Isotherms and Metal Dispersion

The adsorption isotherms for the 2% Pt, Rh, and Pd on alumina catalysts obtained by the elution technique as described above are shown in Figs. 4, 5, and 6. The pressure range in these measurements was limited at the upper end (~80 Torr) by deviations from a linear detector response and at the lower end (~1 Torr) by the sensitivity of the detector. Except for palladium at the two lower temperatures, all isotherms show a strong pressure

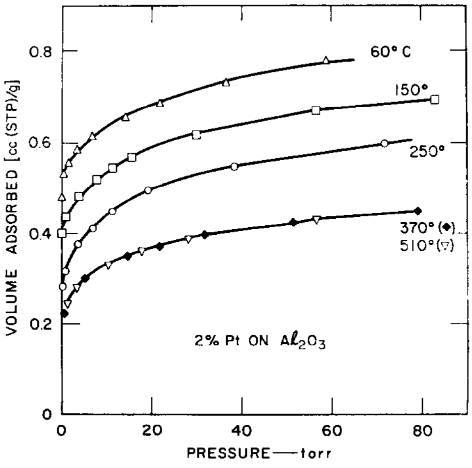

FIG. 4. Adsorption isotherms on 2% Pt/Al_2O_3.

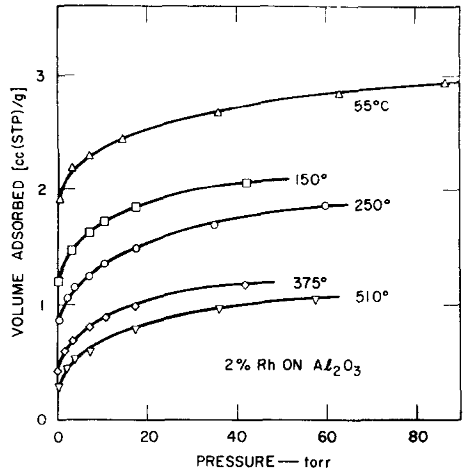

FIG. 5. Adsorption isotherms on 2% Rh/Al_2O_3.

dependence below about 10 Torr, but only a small increase in adsorption between 10 and 80 Torr. In no case was a true saturation reached in this pressure range.

Since there was no measurable adsorption of hydrogen on the support blanc over the whole temperature range and since migration or surface diffusion of hydrogen onto the alumina as reported by Sancier and Inami (*21*) is too slow to affect the elution measurements at temperatures below 300–400°C, the 60–250°C isotherms represent "net adsorption" on the metal and the pressure dependence cannot be ascribed to the support. Thus the intercept method of extrapolating the straight portion of the isotherm to zero pressure, as used by several authors (*10*, *25*) to obtain adsorption values which are representative for the metal dispersion, is not applicable to our measurements. As is shown in Fig. 7, our data can be fitted well to a dissociative Langmuir isotherm over a pressure range of nearly two orders of magnitude. In order to facilitate comparison with static data obtained at higher pressures, we have therefore calculated saturation values (v_m) from the Langmuir isotherms. This is meant strictly as an operational procedure of extrapolation and should not imply validity of true Langmuir kinetics. Certainly at the low pressure end of the isotherm, where effects of surface heterogeneity are most pronounced, deviations from a Langmuir isotherm are to be expected and are also indicated by the data in Fig. 7.

The calculated v_m-values are about 10–30% larger than the experimental values at 50 Torr. They are shown in Fig. 8 for rhodium and platinum together with the isobars for 50 Torr and for $p < 1$ Torr (v_{irr}). For the sake of clarity the data for palladium were omitted from the graph and adsorption is expressed in terms of the ratio H/M (hydrogen atoms adsorbed per metal atom in the sample). In qualitative agreement with the isobaric data summarized by Mears and Hansford (*11*) and the data of Wilson and Hall (*25*), the surface coverage varies strongly with temper-

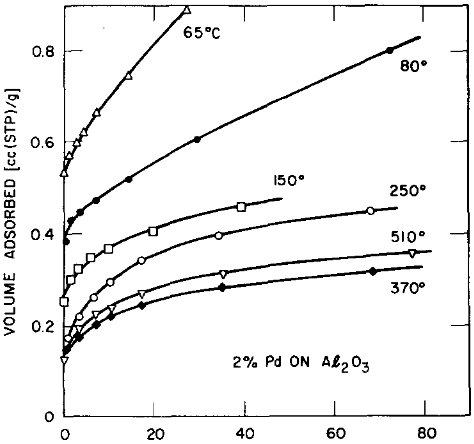

FIG. 6. Adsorption isotherms on 2% Pd/Al_2O_3.

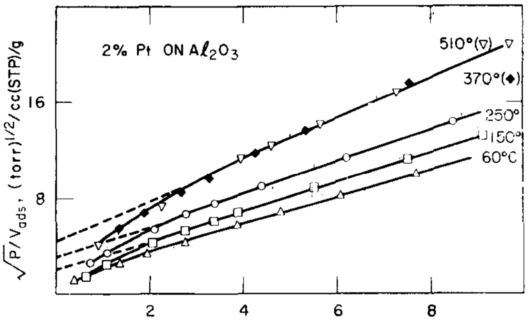

FIG. 7. Langmuir plots of hydrogen adsorption on supported Pt.

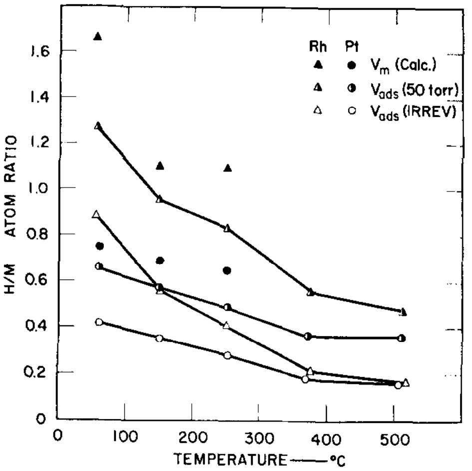

FIG. 8. Summary of adsorption data from elution measurements.

ature, especially at the lower pressures. The calculated v_m-values show a somewhat lesser temperature dependence but still follow the same general trend. Thus, while adsorption on platinum at room temperature in the low pressure range may exceed the 250°C values by as much as 50%, the difference is only in the order of 10% for the high pressures or saturation values. In no case did we find H/Pt ratios greater than 1. For rhodium however, adsorption at 60°C and 50 Torr as well as the calculated v_m for 60, 150, and 250°C were greater than one. In principle this high hydrogen uptake could be due to incomplete reduction or to rhodium being an extremely efficient promoter for hydrogen transfer to the support. The first possibility is unlikely in view of the rigorous pretreatment conditions, the second possibility in view of the fact that the adsorption decreases strongly with increasing temperature. We therefore believe that the high H/Rh ratios are real and due to the different surface properties of rhodium as indicated also by the high carbon monoxide uptake of rhodium catalysts (*4*).

The agreement between adsorption data from the elution measurements and from other techniques is satisfactory. Thus, for the 3 samples containing 2% metal (data shown in Fig. 4, 5, and 6) the volume ratio of hydrogen to carbon monoxide uptake* varied between 0.65 and 1.0 in general agreement with values reported by several authors (*2, 10, 25, 26*). For the 0.5% Pt/Al_2O_3 sample a v_m of 0.23 cc(STP) of hydrogen was calculated from the 250°C elution isotherm, while 0.24 cc(STP) were adsorbed volumetrically at 250°C and 200 Torr (*15*).

CONCLUSION

Chemisorption isotherms can be measured by analysis of the shape of single gas chromatographic elution peaks in combination with a slug difference technique. The method can be applied to the determination of metal dispersion in supported metal catalysts. This application is particularly attractive because at temperatures up to 250°C, the measurements give directly the net adsorption on the metal, thus eliminating any requirements for support corrections and avoiding the uncertainties connected with such corrections. Data obtained with four different catalysts are in general agreement with dispersion values from other adsorption techniques, but show a strong variation with temperatures and a definite dependence on pressure. Therefore, comparison of dispersion data obtained under different experimental conditions is rather difficult. It appears that the fair agreement between hydrogen adsorption at 25°C extrapolated to zero pressure (*25*) and at 250°C and a pressure of 200 Torr is a fortuitous one. The variation of coverage with temperature in the range from room temperature to 250°C is most pronounced at the lower pressures. It decreases with increasing pressure and may amount to only 10–20% at pressures above 200 Torr. However, even the calculated v_m-values still show a small but definite temperature dependence.

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