JOURNAL OF CATALYSIS 1, 85-92 (1962)

The Determination of the Free-Metal Surface Area of Palladium Catalysts

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Received October 31, 1961

Two methods are indicated for the determination of the metallic part of the total surface area of palladium-on-carrier catalysts from the chemisorption of carbon monoxide at room temperature. These methods are particularly suitable for use with a range of metal dispersions and/or concentrations in which measurements by other techniques, e.g., X-ray line broadening, small-angle scattering, and electron microscopy, cause difficulties.

In cases where different techniques were suitable, good agreement was found with the results of carbon monoxide adsorption.

Factors which may lead to erroneous results in the adsorption technique are the presence of residual oxygen or hydrogen on the palladium surface, and, in rare instances, sorption of carbon monoxide on the carrier.

In the case of a 0.5% Pd-on-carrier catalyst the metal appeared to be so highly dispersed on the support that the ratio of adsorbed carbon monoxide molecules to palladium atoms was almost equal to unity.

I. INTRODUCTION

Palladium-on-carrier catalysts have found wide application in reactions in which molecules are partly hydrogenated, for instance, in the selective hydrogenation of acetylene to ethylene (1) and of nitric acid to hydroxylamine (2). To gain an impression of the qualities of the different types of catalyst available on the market, it is necessary not only to test them under process conditions but also to characterize them by measuring the total and free-metal surface areas.

In the past chemisorption was often used to determine surface areas. Emmett and Brunauer (3), for instance, determined the free-iron part of the surface of ammonia synthesis catalysts from the chemisorption of carbon monoxide. Hydrogen chemisorption was successfully applied, for instance, by Schuit and van Reyen (4) in measuring the metallic part of the surface area of nickel-on-carrier catalysts. More recently Spenadel and Boudart (5) reported on the use of hydrogen chemisorption for the determination of the specific surface area of platinum dispersed on an alumina support. Here a difficulty was encountered in that not only chemisorption took place but also hydrogen was taken up in the bulk of the metal, which resulted in an uncertainty of ca. 10% in the final surface area.

In palladium metal much larger amounts of hydrogen are easily dissolved, which completely rules out the use of this gas for standard chemisorption techniques.

As absorption in the bulk metal is fully excluded for CO molecules, the chemisorption of this gas was chosen as a method for comparing metal surface areas of Pd catalysts on various carriers obtained from different sources.

The good adsorbability of carbon monoxide follows from the work of Taylor and McKinney (6), who noted a heat of chemisorption of 15 kcal/mole at full coverage for CO on Pd, and from the research of Stephens (7), who found a rapid CO chemisorption on Pd films at room temperature and 10^{-2} mm pressure up to a coverage $\theta = 0.95$. Hence, at room temperature the chemisorption equilibrium leans heavily toward the side of the adsorbed phase.

In this article we shall report on a procedure in which the Pd surface is calculated from the extent of the chemisorbed CO layer at room temperature. It will be shown, however, that in applying this rather simple procedure some disturbing effects may arise which are difficult to recognize and can lead to rather large errors in the final result.

II. Experimental Procedure

A volumetric glass system as normally applied for surface area determinations (Brunauer-Emmett-Teller method) was used for measuring the total surface area of the samples from the physical adsorption of nitrogen or methane, and the CO adsorption isotherms. For the surface area of a nitrogen molecule Livingston's value of 15.4Å^2 was accepted, which, from measurements on one surface, leads to a value of 16.0Å^2 for the methane molecule.

Titrimetric determinations of the carbon dioxide content of oxygen were carried out with the help of a piston burette filled with $0.02\,N$ sodium methanolate dissolved in a mixture of 75% pyridine and 25% methanol; the indicator was thymol blue.

The gases used were: helium (99.6%) for dead-space determinations; highly purified nitrogen, methane, and carbon monoxide for surface-area determinations; palladium-diffused hydrogen for reduction; and commercial oxygen, freed of H_2, CO, and CO_2 by passing it first through vessels filled with Deoxo catalyst (from Baker) and Ascarite and then through a trap cooled with liquid oxygen.

To have an independent check on our results the mean crystallite size was controlled in suitable cases by the methods of X-ray line broadening and small-angle scattering, and by electron microscope determinations. This work was carried out in the Crystallographic Department of the Central Laboratory.

For the determination of the average palladium crystallite size from X-ray line broadening, the breadth of the (111) X-ray diffraction line was recorded on a Philips diffractometer. The standard equation of Patterson (8), with Jones's (9) corrections, was used in the calculations. The small-angle scattering work was done with a two-crystal spectrometer. The calculations were carried out by the method of Fankuchen and Jellinek (10).

The electron-microscope photographs were made with a Siemens Elmiskop after ultramicrotome sections had been made of the catalyst samples.

The adsorbents or catalysts used were:

Sample A. Palladium black, supplied by Drijfhout & Co., Amsterdam.

Analysis: Ag, Cu, Na, Ca, Pb $<0.01\%$
C: 0.1%

Sample B. Palladium sponge, spectrographically standardized, from Johnson, Matthey & Co. Ltd., London.

Rh: 5 ppm
Si: 3 ppm

Sample C. γ-Al_2O_3, prepared according to Larson (11). Traces of Fe and Cu only.

The commercial Pd catalysts were:

Sample D. 0.47% Pd dispersed on γ-Al_2O_3.

Sample E. 1.1% Pd dispersed on γ-Al_2O_3.

Sample F. 5.5% Pd dispersed on γ-Al_2O_3.

Sample G. 4.9% Pd dispersed on active carbon.

Sample K. 10% Pd dispersed on kieselguhr.

Sample H. 10% Pd dispersed on active carbon.

III. Results

The Determination of the Volume of Chemisorbed Carbon Monoxide

Method α. By way of example Fig. 1 gives the carbon monoxide adsorption isotherms for sample F. After evacuation at 300°C for 20 hr, isotherm *a* was measured at 20°C. At this temperature the gas is bound both physically and chemically. In the measurement of the first two points of isotherm *a*, full adsorption equilibrium was attained after 36 hr, whereas at higher pressures a few hours sufficed to produce equilibrium.

It appeared that, after equilibration, the carbon monoxide contained CO_2. The same effect was observed in the study of samples of pure palladium and palladium dispersed on silica or carbon; only after reduction with hydrogen or after heating *in vacuo* above 500°C, was CO_2 evolution absent. Obviously this carbon dioxide is formed by a reaction of carbon monoxide with oxygen adsorbed on the palladium surface. Removal of oxygen by reduction with hydrogen and subsequent measurement of the CO isotherms presents difficulties, because the high temperatures needed to remove the chemisorbed hydrogen by evacuation cause sintering of the highly dispersed samples (see following sections). Therefore the amount of CO_2, both in the gas phase and physisorbed on the surface,* has to be determined.

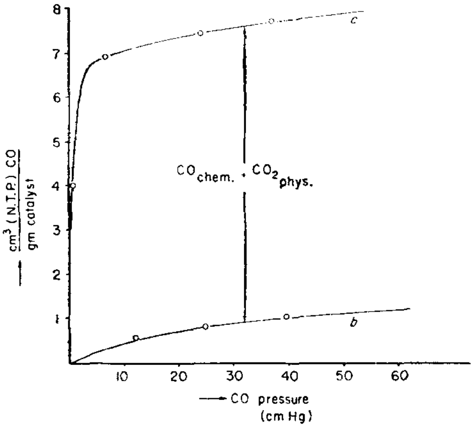

FIG. 1. Adsorption isotherms of carbon monoxide on a sample of 5.5% Pd dispersed on γ-Al_2O_3. $T \simeq 20$°C. Isotherm *a*, chemisorbed CO plus physisorbed CO and CO_2; isotherm *b*, physisorbed CO. The total amount of CO_2 evolved was 0.88 cm^3 (NTP); the physisorbed amount, 0.45 cm^3 (NTP).

The carbon dioxide was frozen out in a U-tube, placed between adsorption vessel and pumping aggregate and cooled with liquid nitrogen, after which the apparatus was evacuated at 20°C for half an hour. The total amount of CO_2 was determined from the known volume of the apparatus and from the pressure increase on warming up of the U-tube to room temperature, with the stopcock of the adsorption vessel closed. Then the stopcock of the evacuated adsorption vessel was opened and the amount of physically adsorbed CO_2 was found from the pressure decrease. This amount is equal to the adsorbed portion of carbon dioxide present in the measurement of isotherm *a*. (The mutual influence of physical CO and CO_2 adsorption is neglected.)

Next, the catalyst vessel and the adsorption apparatus were evacuated at room temperature for half an hour, after which isotherm *b* was determined at 20°C. After repeated pumping at room temperature this isotherm was reproducible; it obviously represents the physically bound carbon monoxide.

Starting from $p_{CO} \simeq 10$ cm Hg, isotherm *b* proved to run at a constant distance under isotherm *a*. It follows that the slope of isotherm *a* above this pressure is only produced by physical CO adsorption, whereas the physical carbon dioxide adsorption remains constant in this pressure range. This is caused by the fact that the formation of CO_2 died away rapidly already at low CO pressure, as was also observed by Stephens (7) at room temperature.

The volume of chemisorbed carbon monoxide was found by subtracting the determined volume of physisorbed carbon dioxide from the volume represented by the distance between isotherm *a* and *b* (see Fig. 1). From the *total* amount of CO_2 evolved, the oxygen coverage on the Pd surface was calculated.

Method β. It proved also possible to determine the amount of chemisorbed carbon monoxide titrimetrically. The evacuated samples were brought into contact with CO under a pressure of $\frac{1}{2}$ atm for 40 hr, after which the physically bound CO and CO_2 were desorbed by pumping for 1 hr. Then pure oxygen was led over the samples at the rate of 5 liters/hr for 5 hr, the temperature of the sample being gradually in-

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* Carbon dioxide is not chemisorbed appreciably by palladium (12).

creased to 300°C. Carbon dioxide, which is evolved according to the surface reaction

$$xO_2 + \mathrm{Pd[CO]_{ads}} \rightarrow \mathrm{Pd}(O_2)_{x-1/2} + CO_2$$

was determined titrimetrically. Above 300°C, CO_2 evolution stopped.

In most cases it was necessary to run a blank, as most carriers contain some carbon which is also converted to CO_2.

The two methods gave results in good agreement with each other, as will be shown in the following.

Determination of the Free-Pd Surface Area Corresponding to 1 cm^3 (NTP) of Chemisorbed CO

In order to be able to calculate Pd specific surface areas from CO chemisorption data, surface area determinations were carried out on two different samples of pure palladium both by physisorption of N_2 or CH_4 at −196°C and by chemisorption of carbon monoxide at room temperature.

The results are summarized in Table 1.

TABLE 1

SURFACE AREA OF PURE PALLADIUM SAMPLES, CALCULATED FROM PHYSICAL ADSORPTION (BET METHOD) AND FROM CARBON MONOXIDE CHEMISORPTION, WITH 1 CM^3 (NTP) CARBON MONOXIDE EQUALIZED TO 3.2 M^2 PD

		Surface area (m^2 Pd/g Pd)		
			From CO chemisorption	
Sample	Pretreatment	From phys. adsorption	Method α	Method β
A. Pd-black	4 hr heating *in vacuo* at 60°C	19.8	19.4	20.5.
B. Pd-sponge	17 hr heating *in vacuo* at 484°C	0.34[a]	0.35	0.30

[a] An electron microscope determination gave a value of 0.32 m^2 Pd/g Pd.

If 1 cm^3 (NTP) of chemisorbed CO is equalized to 3.2 m^2 of palladium, both methods are in good agreement with each other. Moreover, for sample B there was excellent agreement with the electron-microscope determination of the surface area from the observed mean particle size.

Characterization of Commercial Samples

Table 2 gives a compilation of the results obtained with a series of commercial catalyst samples. The palladium surface areas were calculated on the basis just described. The mean crystallite sizes were calculated from these surface areas on the assumption that cubic particles are present, the faces of which are all accessible.

Separate experiments proved that pure γ-Al_2O_3 did not show any CO chemisorption after 20 hr of heating *in vacuo* at 300°C. Pumping at 500°C for 20 hr, however, resulted in the adsorption of a small amount of carbon monoxide (0.1 cm^3 (NTP)/100 m^2 Al_2O_3) not desorbable on pumping at room temperature, which is in accordance with the results of Menon (13). Corrections for this sorption have to be made in particular in dealing with Al_2O_3 carriers with a low Pd content, preheated at 500°C and above.

Table 2 gives also the experimental results for a 0.47% Pd-on-γ-Al_2O_3 catalyst after pretreatment at different temperatures; here sintering of the Pd crystallites appears to become of importance on heating at 300°C.

In cases where the adsorption results could be checked by means of other techniques, good agreement was found. The results from the X-ray line-broadening technique are about 30–40% higher than the others. This technique, however, gives the weight mean diameter d_w, represented by (14)

$$d_w = \sum_i n_i d_i^4 / \sum_i n_i d_i^3$$

where n_i is the number and d_i the diameter of the *i*th particle, whereas the adsorption method leads to the mean volume-surface diameter d_{vs} (14),

$$d_{vs} = \sum_i n_i d_i^3 / \sum_i n_i d_i^2$$

TABLE 2

SURFACE AREAS AND PD CRYSTALLITE SIZES OF SOME COMMERCIAL PD-ON-CARRIER CATALYSTS

Sample	Pretreatment evacuation		Method	Total surface area (m²/g catalyst)	Pd surface area (m² Pd/g Pd)	Oxygen [cm³ O_2 (NTP)/m² Pd]	Mean crystallite size (Å) from			
	Temp. (°C)	Time (hr)					CO adsorption	X-ray line broadening	Small-angle scattering	Electron microscopy
D. γ-Al_2O_3 + 0.47% Pd	100	20	α	122	595	0.0	8.4	—	—	14
	300	20	α	129	454	0.0	11.3	—	—	—
	500	20	α	129	150	0.0	33.0	—	—	47
E. γ-Al_2O_3 + 1.1% Pd	100	20	α	119	337	0.0	15.0	—	—	—
	300	20	α	119	311	0.0	16.0	—	—	—
F. γ-Al_2O_3 + 5.5% Pd	300	20	α	234	364	0.03	13.7	—	—	—
	300	20	β	234	326	0.0	15.3	—	—	—
	500	48	α	233	107	0.0	47.0	52[a] (±10)	—	—
G. Carbon + 4.9% Pd	100	20	α	1000	131	0.38	38.0	—	—	—
	300	20	α	1000	121	0.0	41.5	57[a] (±10)	—	—
H. Carbon + 10% Pd	300	20	α	1250	151	0.06	33.0	46[a] (±10)	—	—
K. Kieselguhr + 5% Pd	300	20	β	38	45	0.0	112	163[a] (±30)	108, 154[a]	—

[a] Weight mean diameters; the other values are mean volume-surface diameters.

The d_w is always higher than d_{vs}, the difference depending on the particle size distribution.

From the small-angle scattering technique a distribution of particle sizes results, and, hence, both d_w and d_{vs} can be calculated from the results obtained with this technique. We see from Table 2 that for sample K the weight mean diameter is in good agreement with the result of the line-broadening technique and the mean volume-surface diameter with that of the adsorption method.

The amounts of adsorbed oxygen calculated from the amounts of CO_2 evolved are also indicated in Table 2. On pumping at 300°C or higher, virtually all oxygen is desorbed. It is not yet clear why the γ-Al_2O_3 samples with 0.47 and 1.1% Pd did not give rise to CO_2 formation after pretreatment at 100°C.

Influence of a Hydrogen Treatment on the Extent of the Carbon Monoxide Adsorption

In separate experiments the influence of the preadsorption of hydrogen and the evacuation at different temperatures was investigated.

From Table 3 it appears that on heating of a Pd-on-alumina catalyst in hydrogen and pumping at 100 or 300°C for 20 hr the chemisorbed amount of CO is appreciably lowered. It is clear that evacuation at 300°C for 20 hr is not sufficient to remove the hydrogen completely. Pumping at higher temperatures may cause appreciable sintering of the Pd crystallites, as already indicated.

TABLE 3

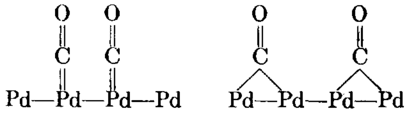
THE INFLUENCE OF HYDROGEN ON THE EXTENT OF THE CARBON MONOXIDE CHEMISORPTION ON PALLADIUM (SAMPLE E. 1.1% PD DISPERSED ON γ-ALUMINA)

Heating in hydrogen		Additional heating *in vacuo*		
Time (hr)	Temp. (°C)	Time (hr)	Temp. (°C)	Chemisorbed CO [cm³ (NTP)/g Pd]
0	0	20	100	105.3
20	100	20	100	46.3
0	0	20	300	97.3
20	300	20	300	59.0

IV. DISCUSSION

The CO chemisorption experiments on pure palladium samples pointed to adsorption of 1 cm³ CO on 3.2 m² Pd surface area, or 0.86×10^{15} CO molecules/cm² Pd. It is interesting to compare this number with the results of modern fundamental chemisorption studies.

According to Laneyon and Trapnell (15) and to Couper and Eley (16) 1.2×10^{15} Pd atoms/cm² of palladium surface area are present; this is the mean value for the crystallographic planes (100), (110), and (111). Concerning the mode of binding of carbon monoxide on palladium, Eischens *et al.* (17) in their IR study of this chemisorption system observed two major bands in the spectrum which were assigned to the presence of "linear" and "bridged" carbon monoxide on the surface:



(linear) (bridged)

The bridged CO is the more strongly bound species; the IR band of this group disappeared last on desorption.

Combining these data, it follows from our experimental figure, that 50% must be present in the linear and 50% in the bridged form. This result is compatible, though not in full agreement, with the estimation of Stephens (7), who observed that ca. 70% of the CO on Pd is converted rapidly to CO_2 on reaction with oxygen and 30% slowly. He concluded from this that 30% is present in the strongly bound, bridged, form.

In dealing with crystallites of very low mean-particle size, for instance <30Å, the possibility that the CO/Pd ratio at full coverage may change cannot be ruled out. First, the ratio between the number of different crystallographic planes may change, and second, every plane may have its own "bridged-to-linear" ratio. Therefore, the absolute values of the free-Pd surface area calculated for samples with such small crystallites must be viewed with some reserve, but they can at all events be used for the purpose of comparison.

In the case of the Pd-on-alumina catalysts (see Table 2), the dispersion of palladium is extremely high. Here calculation shows that, for the 0.47% Pd-on-alumina catalyst, 0.88 CO molecule is chemisorbed per Pd atom (bulk plus surface-Pd atoms). Such an extreme dispersion was also observed by Spenadel and Boudart (5) in the case of hydrogen chemisorption on a 0.6% Pt-on-alumina sample, viz., 1($\pm$10%) H atom per platina atom. Hence, the palladium atoms may be present in an atomically dispersed form or as two-dimensional clusters, but the presence of normal three-dimensional crystallites is certainly not ruled out [Spenadel and Boudart (5)]. Crystallites composed of eight unit cells ($d \approx 11$Å), for instance, are built up of 63 atoms, 50 of which are present as surface atoms, and hence such crystallites may well be responsible for the high CO/Pd ratio observed.

An electron-microscope study of ultramicrotome sections of a 0.47% Pd-on-alumina catalyst threw some light on this problem. The use of a high-resolution technique made visible crystallites with a mean volume-surface diameter of 14Å in the case of a sample pumped at 100°C for 20 hr, whereas from CO adsorption 8.4Å was found. Further investigations with even higher resolution are now in progress† and perhaps still smaller crystallites will then become visible, but, in any case, the largest part of the Pd seems to be present as normal crystallites and not in an atomically dispersed form. The mean volume-surface diameter found for the Pd crystallites in the same catalyst after pumping at 500°C for 20 hr is in reasonable accordance with the result from the adsorption work (see Table 2).

In the case of Pd on alumina, practically the whole surface of the carrier is formed by pores with a radius of 40–60Å. The diameter of the Pd crystallites is smaller and, hence, we may expect them to be present in the whole pore system. For Pd on carbon the situation is different (see Table 2). The crystallites, with a diameter of 30–40Å, do not fit in the pores, the diameter of which estimated by Joyner's method (18) amounts to ca. 20Å.

A study of the pore-size distribution of active carbon showed that, besides the system of micropores which largely determines the surface area, a system of medium-size pores exists with radii between 20 and 1000Å, so that it is likely that the palladium crystallites will chiefly occur in this last system. The reason why they do not occur in the micropores may be that during the preparation of the catalysts only the large pores became wetted by the palladium chloride solution, owing to the hydrophobic character of active carbon.

Table 3 shows the influence of hydrogen treatment on the CO chemisorption, which is so large that, by applying reduction previous to the determination of the free-Pd-surface area from CO chemisorption, serious mistakes can be made. The origin of the effect must be sought in the strongly bound hydrogen on the palladium surface (19), which even after 20 hr of pumping at 300°C suppresses the extent of the CO chemisorption to 80% of its original value.

The same effect was observed by us in the case of hydrogen chemisorbed on nickel (20). Here it appeared from a gravimetric determination that after 20 hr of pumping at 300°C, 15% of the hydrogen monolayer was still on the surface.

ACKNOWLEDGMENTS

We wish to express our appreciation to Mr. P. Zwietering and Dr. R. Westrik for helpful discussions relating to this work. Further thanks are due Dr. C. G. Vonk and Dr. J. A. Cras for making the line-broadening and small-angle scattering measurements and to Mr. A. M. Kiel, who carried out the electron-microscope study of ultramicrotome sections of some catalyst samples.

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† A more detailed report of the electron-microscope investigation will be published by R. Westrik and A. M. Kiel.

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