

## The Structure and Activity of Supported Metal Catalysts

### VI. Measurement of Dispersion in Palladium-Charcoal Catalysts

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The metal dispersion in Pd-charcoal catalysts can be estimated from X-ray line-broadening and intensity measurements (yielding respectively, mean crystallite sizes and the percentage of Pd detectable, i.e., due to crystallites greater than 50 Å size) thereby preserving the high dispersion existing after catalyst manufacture. The theoretical X-ray intensity and intensities from sintered samples relative to an internal standard, MgO, are compared and discussed. Surface cleaning, the normal prerequisite for chemisorption measurements, although very mild in this case (H<sub>2</sub> at 25°C; evacuation at 100°C), can induce sintering, particularly at high Pd contents or with nonuniform Pd distributions over the charcoal support. Despite the mild pretreatment, amounts of CO subsequently chemisorbed were consistent with information from X-ray diffraction and electron microscopy. The observed Pd atoms (exposed)/CO molecules (adsorbed) ratios obtained for sintered and high dispersion Pd-charcoal catalysts are discussed.

#### INTRODUCTION

The measurement of metal area, or the degree of metal dispersion, seems particularly difficult for palladium-charcoal catalysts compared with, say, platinum-silica catalysts. Often with supported Pt catalysts, the Pt surface is cleaned by gas-phase H<sub>2</sub> reduction; the H<sub>2</sub> desorbed by evacuation at high temperatures and then either H<sub>2</sub> or CO chemisorbed on the metal under conditions which minimize adsorption on the support. While the value and constancy of the ratio, metal atoms (exposed)/H<sub>2</sub> or CO molecules (adsorbed), assumed in calculating the metal area is still open to discussion, nevertheless a useful measure of metal dispersion is obtained. In contrast, the sorption of H<sub>2</sub> in palladium and especially sintering induced by the prechemisorption treatment may introduce uncertainty into the determination of Pd areas in Pd-charcoal catalysts.

Scholten and van Montfoort (1) avoided the use of H<sub>2</sub> (for either cleaning the Pd surface or for chemisorption) by degassing

at 300°C, adsorbing CO, and taking account of CO<sub>2</sub> formation, due to reaction with surface oxygen, while Kral (2) reduced Pd-charcoal catalysts at 200°C before CO adsorption. Recently Aben (3) using calcined Pd-silica and Pd-alumina catalysts, reduced and evacuated at 400°C, demonstrated that suitable conditions could be found for H<sub>2</sub> chemisorption.

The present work is concerned with Pd area measurements in highly dispersed Pd-charcoal catalysts commonly used in liquid-phase hydrogenation processes. High temperatures cannot be used for surface cleaning or for H<sub>2</sub> removal after reduction, and the following approach was adopted: The Pd dispersion was determined from the X-ray line-broadening, but it was recognized that much of the Pd might be present as very small crystallites which would remain effectively 'X-ray amorphous', and hence the fraction of Pd contributing to the mean crystallite size was also determined. This information was used to indicate changes in dispersion

which sometimes occur when the Pd-charcoal catalysts are reduced in  $H_2$  and outgassed even under mild conditions and to point out how this apparent sintering is related to Pd content, distribution, etc.

It was then of interest to discover the extent of CO adsorption on Pd-charcoal catalysts outgassed at temperatures which might be thought insufficient to desorb the  $H_2$  used in surface cleaning. Finally, using both extensively sintered and high-dispersion Pd-charcoal catalysts, X-ray diffraction and electron microscope observations were combined with chemisorption measurements to investigate the ratio of exposed Pd atoms to adsorbed CO molecules.

## EXPERIMENTAL

### *X-ray Diffraction*

About 0.07 g of catalyst and about 0.007 g of roasted MgO were weighed into a boron carbide crucible and ground together for 5 min. The resulting mixture was then made into a flat layer on a cover slip and mounted on the sample stage of a Philips PW 1050 goniometer fitted with a krypton proportional counter. Profiles of the Pd (111) and MgO (200) reflections were recorded at an angular speed of  $1/8^\circ$  ( $2\theta$ )/min and at a chart dispersion of 8 or 16 cm/deg. Background intensities were estimated from the level regions of the wings of the profiles and peak areas measured with a planimeter. As discussed later, these peak areas were used to estimate the fraction of Pd detectable by X-ray diffraction and contributing to the observed mean crystallite size. Crystallite sizes were calculated from the profile width at one-half its maximum height, using the standard Scherrer equation and the classical value of the Scherrer constant,  $K = 0.90$  and correcting for instrumental broadening using Warren's expression as previously (4).

### *Electron Microscopy*

Catalysts were examined as thin sections cut on an ultramicrotome. The sample was prepared for cutting by setting

it in the end of a block of 'Araldite' resin. Tests were carried out to show that the setting temperature (60–80°C) did not cause any sintering of the dispersed palladium (as observed by X-ray diffraction). The electron microscope used had a rated best-line resolution of 4.5 Å; with the present samples, the typical point resolution would be 10 Å.

### *CO Chemisorption*

A conventional volumetric apparatus was used with a single bulb burette of ~35 ml capacity and incorporating greaseless stopcocks with Viton A diaphragms covered with PTFE where necessary. Pressures were measured with miniature Pirani gauges operated at constant filament temperature with self-balancing control units. The whole system was enclosed in a cabinet thermostatted at 33°C. Unless otherwise stated, the following standard procedure was used: The sample, usually ~0.3 g-catalyst contained in a glass tube, was glass-blown on to the equipment, and air was removed by evacuation or by purging with pure nitrogen or helium. Hydrogen at atmospheric pressure was passed over the sample (100 ml/min) at 25°C for 2 hr; hydrogen was pumped out, the temperature raised to 100°C, and the catalyst evacuated overnight. The catalyst was then cooled to 33°C, the dead-space determined with helium, and after evacuation, doses of CO were adsorbed. 'Blank' experiments with the charcoal support showed a negligible contribution to the observed adsorption on the catalysts.

### *Materials*

Hydrogen was purified by diffusion through a silver-palladium membrane, carbon monoxide and helium were 'Spectroscopically pure' gases (British Oxygen Co. Ltd.) supplied in Pyrex vessels.

Catalysts were supplied by Johnson Matthey and Co. Ltd. and were research grades of standard types. Similar catalysts prepared on Darco G60 are identified by type numbers A2, B2, and C2.

## RESULTS AND DISCUSSION

*X-ray Intensity Measurements*

The observed X-ray diffraction intensities were often lower than expected, indicating that after preparation the Pd-charcoal catalysts must contain substantial amounts of highly dispersed palladium which does not contribute to the X-ray diffraction result. Electron micrographs confirm the high metal dispersion in many catalysts. Therefore, the quantitative determination of the fraction of Pd detected by X-ray diffraction is valuable additional information on metal dispersion. In the absence of such information, average crystallite sizes obtained by X-ray line-broadening are not meaningful, because only a small fraction of the palladium present might be represented. Further, where X-ray data are used to calculate the palladium areas in catalysts, even a small amount of undetected palladium will cause a serious error, because it makes a disproportionate contribution to the total palladium area.

The fraction detectable by X-ray diffraction was found by comparing the intensity of radiation scattered from the 'unknown' catalyst sample with that from a standard sample where all the metal is believed to be detectable. In principle, a simple substitution method might be used to make the comparison, i.e., the intensity of the metal (111) peak, is recorded from the unknown catalyst sample and the operation repeated with the standard material. The instrumental conditions must be assumed constant over the period of the experiment. Even more important considerations are that the amount of metal and the area irradiated must also be kept constant and that the sample is effectively infinitely thick with respect to X-rays. Therefore, the comparison was made using an *internal* standard, magnesium oxide, which is stable, readily available in finely divided form, and has a simple fcc lattice whose (200) reflection falls close to, but does not overlap with the (111) reflection of palladium.

The catalyst sample to be examined was

mixed in a known and constant proportion with MgO and the intensity ratio  $\alpha$ , determined where

$$\alpha = \frac{\text{Area Pd (111)}}{\text{Area MgO (200)}}. \quad (1)$$

The observed value of  $\alpha$  was adjusted to a reference system containing 4.5% Pd and 10% MgO by weight, which was convenient for the present work. Then, if the value of  $\alpha$  is known for a standard catalyst sample, where all the palladium is detectable by X-ray diffraction, (this value is designated  $\alpha_s$ ), adjusted to the same reference system, the fraction of palladium detectable in the 'unknown' catalyst sample can be obtained. The quantity '% Pd detected' in Tables 2-6, is  $100\alpha/\alpha_s$ . The theoretical calculation of  $\alpha_s$  and its experimental determination is discussed below.

The ratio of the intensities,  $\alpha$ , is given by Ref. (5):

$$\alpha = \frac{\text{Area Pd (111)}}{\text{Area MgO (200)}} = \frac{I_1}{I_2} = \frac{p_1 F_1^2 \phi(\theta_1) G_1 V_2 M_2}{p_2 F_2^2 \phi(\theta_2) G_2 V_1 M_1}, \quad (2)$$

where the multiplicity factors,  $p_1$  and  $p_2$ , are 8 and 6, respectively;  $\phi(\theta)$  is the combined Lorentz polarization factor;  $G$  is the mass of component in the mixture; and  $V$  and  $M$  are the volume and molecular weight of the unit cell, respectively. The structure factors  $F$  for these substances are given by

$$F_1 = 4f_{\text{Pd}} \text{ and } F_2 = 4[f_{\text{Mg}} + f_{\text{O}}], \quad (3)$$

where  $f$ , the atomic scattering factor, a function of  $\sin \theta/\lambda$  was obtained from standard tables (6). Adjusted to the usual reference system, (4.5% Pd, 10% MgO) the theoretical value for  $\alpha_s$  is 2.38. Equation (2) ignores the absorption and temperature effects and, of course, assumes that all the material is detectable. However, when MgO and NaF, which have similar absorption coefficients, were mixed together in a molar ratio of 0.8, the calculated and experimental intensity ratios of the (200) reflections in the two substances were in satisfactory agreement, 1.47 and

1.49, respectively. This provided support for the validity of the calculations when particle absorption effects are minimized.

The first approach to an experimental value for  $\alpha_s$  was made using samples of type B2 catalyst containing 5% Pd, which were heated at various temperatures up to  $\sim 900^\circ\text{C}$ , so that the *apparent* mean crystallite size, originally  $<100 \text{ \AA}$ , increased to  $\sim 400 \text{ \AA}$  (Fig. 1). It was expected that the corresponding  $\alpha$  values would tend to a limit when all the metal crystallites had become sufficiently large to be detected. It can be seen from Fig. 1 that  $\alpha$  values leveled out at  $\sim 1.8$ , but exhibit a tendency to decrease again as a result of extreme heat treatment. Table 1 (first line) records the experimental value as 1.79, which is the mean of the three highest  $\alpha$  values observed. Also recorded in Table 1 are experimental  $\alpha$  values for other types of Pd-charcoal catalyst, containing approximately 10% or 20% Pd; (exact Pd contents were determined for samples after firing at temperatures up to  $900^\circ\text{C}$ ). The highest value for  $\alpha_s$  found experimentally, 2.09, was still less than the calculated value of 2.38.

The discrepancy between the calculated and observed values of  $\alpha_s$  might be ascribed to a residue of 'X-ray amorphous'

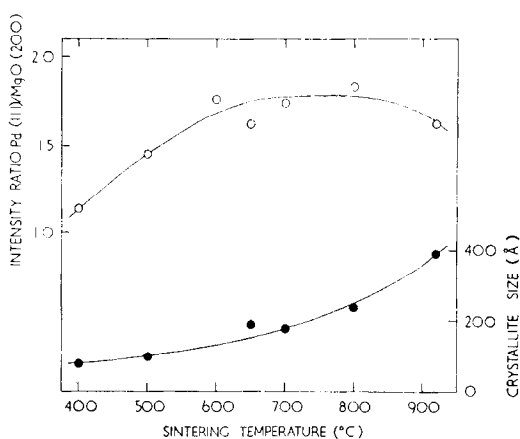


FIG. 1. Effect of sintering temperature on a (nominal) 5% Pd-charcoal catalyst (type B2), with respect to mean crystallite size (●) and X-ray intensity ratio (○), Pd (111)/MgO (200), adjusted to a reference system of 4.5 wt % Pd and 10 wt % MgO.

Pd despite the extreme sintering conditions used. Such finely divided Pd might be trapped within the charcoal support and be incapable of growth by sintering. However, there is evidence that the discrepancy is caused by X-ray absorption effects. The scattered X-ray beam from the component for which the product (linear absorption coefficient)  $\times$  (particle size) is greatest

TABLE 1  
X-RAY INTENSITY RATIOS, Pd (111)/MgO (200)<sup>a</sup>

Sample % Pd	Type	Heat treatment (temp, °C)	Crystallite or Particle size (Å)		X-ray intensity ratio, $\alpha$
			X-ray	CO Ads <sup>a</sup>	
5	B2	vac, 700-920, 20 hr	180-390	—	1.79
		vac, 900, 66 hr	410	—	1.65
		vac, 900, 24 hr	610	—	1.95
10	C2	vac, 760, 22 hr	390	—	1.68
		vac, 900, 24 hr	610	—	1.95
10	B2	vac, 900, 20 hr	390	—	1.66
		vac, 900, 70 hr	460	—	2.09
20	A1	vac, 790, 20 hr	350	—	1.70
Pd black		H <sub>2</sub> , 25°, vac, 100	190	645	2.02
		H <sub>2</sub> , 150°, vac, 140	220	495	1.92
		H <sub>2</sub> , 190°, vac, 190	500	2453	1.57
		H <sub>2</sub> , 25°, vac, 225	560	4540	1.37

<sup>a</sup> Adjusted to wt Pd/wt MgO = 0.45.

will suffer the greatest loss of intensity, and the coefficient for Pd is about 25 times the coefficient for MgO. Therefore, the intensity of the Pd (111) reflection, and hence  $\alpha$  appears to be depressed in all experiments.

Table 1 shows that  $\alpha_s$  determined for a series of Pd blacks decreased as the particle size (determined from CO chemisorption, assuming ratio Pd atoms exposed to CO molecules adsorbed is unity) increased. This decrease in  $\alpha_s$  from 2.00 to 1.37, with increasing aggregate size in Pd black, is strongly suggestive that aggregation of Pd in the sintered Pd-charcoal catalysts is also the cause of the discrepancy between  $\alpha_s$  (obsd) and  $\alpha_s$  (caled). Furthermore, absorption coefficients and hence the magnitude of particle size effects depend on the wavelength of the incident X-rays; therefore by changing the X-ray tube it should also be possible to change  $\alpha_s$ , if particle size effects are operating. Using Cu  $K\alpha$ , Co  $K\alpha$ , and Cr  $K\alpha$  radiations, a series in which the wavelength increases from 1.54 to 2.29 Å, the value of  $\alpha_s$  (obsd) for a type B2 catalyst decreased from 1.77 to 1.47. The theoretical value of  $\alpha_s$  is nearly independent of wavelength, but it is clear that the observed values in this case show a strong dependence, decreasing as the wavelength and particle absorption coefficients increase. This is additional evidence that absorption effects are responsible for the discrepancy between the theoretical and observed values of  $\alpha_s$ .

The mean value for  $\alpha_s$  for all the Pd-charcoal catalysts in Table 1 is 1.79, and this value has been used throughout subsequent sections of this work. Palladium areas were calculated from the X-ray data, assuming that the crystallites were cubes exposing 5 faces, and in Tables 2-4, it has been assumed that the mean size of the 'X-ray amorphous' palladium is 25 Å. It should be noted that these tables are essentially illustrative of the extent of sintering, because nothing is known about the behavior of this 'X-ray amorphous' palladium, but the decrease in Pd area shown must be the minimum amount.

### *Sintering During Pretreatment for CO Chemisorption*

In many of the catalysts used in the present work, little palladium metal could be detected by X-ray diffraction immediately after their preparation. This suggests that either the Pd is highly dispersed as crystallites substantially smaller than 50 Å or alternatively the palladium may still be in a highly dispersed unreduced state. Type B1 catalysts are nominally reduced after preparation, but nevertheless, little palladium could be detected in them by X-ray diffraction before gas-phase reduction. Further, a careful search of the X-ray diffraction traces did not reveal any diffraction lines which could be attributed to palladium compounds in type C1 catalysts with 1 and 10% Pd contents. Therefore, it is desirable that the pretreatment of the catalysts before Pd area measurements by CO chemisorption should preserve this high dispersion.

In catalyst pretreatment, air must be removed from the sample and hydrogen admitted to reduce the catalyst and clean the metal surface, and then the hydrogen may be removed by outgassing. However, it was found that apparently very mild pretreatment conditions caused a large increase in the amount of palladium detectable by X-ray diffraction, indicating a loss in Pd area. In the following section, experiments are described which isolate the particular stage in the pretreatment which caused this apparent crystallite growth.

In Table 2, Pd areas were derived from X-ray data primarily because, in a number of instances, the investigation required that only a part of the pretreatment needed for CO adsorption measurement should be carried out. Where CO adsorption measurements were made, it was assumed for comparative purposes that the ratio, Pd atoms (exposed)/CO molecules (adsorbed), was unity. The table shows that the initial removal of air had no effect, but that very mild reduction (25°C for 2 hr) caused the Pd area to decrease by about one-third from its potential value (Expts

TABLE 2  
 CATALYST PRETREATMENT BEFORE CO CHEMISORPTION  
 (10% Pd, type A2)

Experiment	Catalyst pretreatment temp (°C), time (hr, min)	X-ray Data			CO adsorption
		% detected	Crystallite size (Å)	Pd area (m <sup>2</sup> /g-catalyst)	Pd area m <sup>2</sup> /g-catalyst
	Untreated	5	410	15.5	—
1	Purged He, 25°	5	400	15.5	—
2	He, 25°, 45 min; H <sub>2</sub> , 25°, 2 hr	48	95	10.4	—
3	Repeat as above	55	85	10.0	—
4	Evacuate, 25°, 30 min; H <sub>2</sub> , 25°, 2 hr	52	110	9.8	—
5	As above; outgas, 100°, 16 hr	40	100	11.4	—
6	As above; CO adsorption	50	115	10.0	8.0
7	Repeat as above	—	—	—	11.3; 10.9
8	He, 25°; H <sub>2</sub> , 25°, 30 min, increased to 100° over 30 min; H <sub>2</sub> , 100°, 1 hr; outgassed, 100°, 16 hr	—	—	—	10.9

2-4) perhaps as much as, 15-16 m<sup>2</sup>/g-catalyst. However, hydrogen removed by outgassing at 100°C for 16 hr (Expt 5) and subsequent CO adsorption (Expts 6 and 7) did not cause any further loss in Pd area.

Subsidiary experiments showed that reduction at 120°C (again using a type A1 catalyst but with 20% Pd) did not cause any more sintering than would occur during reduction at 25°C. Therefore, a higher reduction temperature than 25°C might be considered in the interests of improving the specific adsorptive capacity of the Pd surface for CO chemisorption. Experiment 8 (Table 2) shows that this is not the case for reduction at 100°C, i.e., 10.9 m<sup>2</sup>/g-catalyst is substantially less than the calculated value of 15-16 m<sup>2</sup>/g-catalyst.

A number of experiments were carried out with the object of minimizing the sintering which can occur at the reduction stage as shown above. Mixtures of 10-20% H<sub>2</sub> in He were used; catalysts in the form of aqueous suspensions were reduced with bubbling hydrogen, and also prolonged evacuation before the standard reduction was tried. However, the extent of sintering as shown by crystallite size and fraction

detectable by X-ray diffraction, was not significantly altered.

#### *Effect of Pd Content*

Table 3 shows crystallite sizes and percent Pd detected in type B1 catalysts prepared on two types of charcoal and containing 1, 5 and 10% (nominal) Pd. Actual Pd contents were used in calculating Pd areas with the usual assumptions. 'After treatment' refers to catalysts examined by X-ray methods after receiving the following preparation; air removed by evacuation or purging with helium; hydrogen reduction at 25°C for 2 hr, outgassing at 100°C for 16 hr. In most cases catalyst pretreatment increased the amount of palladium detected by X-ray diffraction, presumably showing, as discussed above, that crystallite growth had occurred. The corresponding decrease in crystallite size in some catalysts is, at first sight, apparently anomalous but can be ascribed to the sintering together of crystallites smaller than 50 Å in the pretreatment. Thus, these crystallites become detectable by X-rays, thereby decreasing the mean size of the detectable fraction. This effect has

TABLE 3  
EFFECT OF Pd CONTENT ON SINTERING CAUSED BY TREATMENT BEFORE CO ADSORPTION

Catalyst		Before treatment			After treatment			Reduction in Pd area (%)
		Cryst. size (Å)	Fraction detected	Pd area (X-ray diffraction) (m <sup>2</sup> /g-cat.)	Cryst. size (Å)	Fraction detected	Pd area (X-ray diffraction) (m <sup>2</sup> /g-cat.)	
% Pd, (nominal)	Type							
1	B1	100	0.26	1.31	170	0.27	1.26	4
5	B1	115	0.09	8.1	145	0.15	7.6	6
10	B1	110	0.16	14.4	70	0.37	12.5	13
1	B2	200	0.27	1.4	210	0.27	1.4	0
5	B2	195	0.10	7.5	150	0.29	6.2	17
10	B2	190	0.13	14.3	110	0.38	11.4	20

been noted previously (3) for Pd-charcoal catalysts.

The table shows clearly that the percentage decrease in the Pd area caused by the pretreatment stage is insignificant for 1% Pd catalysts but can be more at higher Pd contents. Other catalysts (type C1), in which less Pd was detectable before the pretreatment, sintered much more at the 10% Pd level. For example, no Pd was detected initially in 1% and 10% catalysts, but after pretreatment, while Pd was still undetected in the 1% catalysts, 75% was detected in the 10% catalyst.

#### Effect of Pd Distribution

Further information on the resistance of different types of Pd-charcoal catalysts (with the same Pd content) to sintering during the pretreatment necessary for

chemisorption measurements is given in Table 4. On both types of charcoal, type B1 catalysts sintered least (13–20% loss in Pd area); sintering was more extensive in type A1 catalysts (21–37%) and very extensive with type C1 catalysts (58–67%).

Electron micrographs suggest a possible explanation for the observed differences in sinterability between the extreme cases, types B1 and C1. Figures 2a and b are representative of a large number of observations made on sections of these catalysts. In type B1 (before sintering), the Pd was reasonably well distributed over the charcoal support (Fig. 2a). In contrast, the Pd is concentrated in the type C1 catalyst in certain areas, which can often be associated with the outside of the charcoal granules (Fig. 2b). By analogy, with the effect of Pd content discussed above, sintering must be enhanced by these high

TABLE 4  
EFFECT OF CATALYST TYPE ON SINTERING DURING TREATMENT BEFORE CO ADSORPTION  
(Nominal, 10% Pd)

Catalyst (type)	Before treatment			After treatment			Reduction in Pd area (%)
	Cryst. size (Å)	Fraction detected	Pd area (m <sup>2</sup> /g-cat.)	Cryst. size (Å)	Fraction detected	Pd area (m <sup>2</sup> /g-cat.)	
B1	110	0.16	14.4	70	0.37	12.5	13
B2	190	0.13	14.3	110	0.38	11.4	20
A1	240	0.09	12.8	130	0.32	10.1	21
A2	410	0.05	15.9	115	0.50	10.0	37
C1	<50	0.0	15.6	110	0.75	6.6	58
C2	390	0.06	14.8	210 <sup>a</sup>	0.79	4.9	67

<sup>a</sup> H<sub>2</sub> reduction at 100°C.



FIG. 2. Electron micrographs from ultramicrotome sections of (nominal) 10% Pd-charcoal catalysts: (a) Type B1, showing uniform Pd distribution; (b) type C1, showing localized concentration of the metal, with magnification, 90,000 $\times$ .



local concentrations of metal in type C1 catalysts.

### CO Chemisorption Measurements

The preceding section showed (using X-ray data) that providing the Pd content is not too high and is evenly distributed throughout the charcoal, then H<sub>2</sub> reduction at 25°C and outgassing at 100°C does not seriously sinter the catalyst. It is now necessary to show that Pd surfaces subject to such mild pretreatment will adsorb CO in strict proportion to the area of Pd exposed.

Chemisorption on highly sintered Pd-charcoal catalysts is discussed first, i.e., catalysts fired in vacuum at high temperatures before reduction. In these catalysts, all the Pd is considered to have sintered into crystallites sufficiently large to be detectable by X-ray diffraction. Hence the observed crystallite size (from X-ray line-broadening) provided an immediate estimate of the Pd area. In order to calculate the number of Pd atoms exposed, from the X-ray data, it was assumed that the mean area of each Pd atom exposed was 7.9 Å<sup>2</sup>. The mean number of sites per cm<sup>2</sup> for a fcc metal is given by  $1.91 \times 10^{16}/a^2$ , where  $a$  is the lattice constant (in Å) if equal areas of the three most prominent planes, (111), (100), and (110) are exposed (7), yielding  $1.26 \times 10^{15}$  sites/cm<sup>2</sup> for Pd.

After reduction and evacuation under

the usual conditions CO chemisorbed at 33°C gave standard isotherms with a clear indication of the monolayer coverage; adsorption on the charcoal support was negligible (Fig. 3). Table 5 shows the number of CO molecules adsorbed per gram of

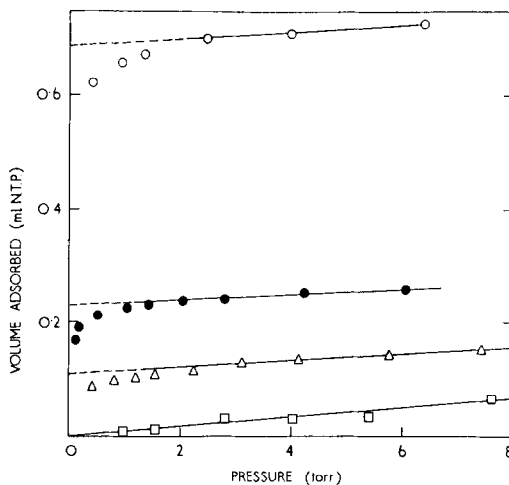


Fig. 3. CO adsorption at 33°C on Pd-charcoal catalysts: ○, 0.297 g, type B1, 5% Pd; ●, 0.645 g, type C2, 10% Pd, sintered at 760°C for 22 hr; △, 0.299 g, type B1, 1% Pd; □, 0.296 g, charcoal support.

catalyst, the number of Pd atoms exposed (from X-ray data), and the ratio, Pd atoms (exposed)/CO molecules (adsorbed). The results are arranged in Table 5 according to the increase in Pd/CO ratio. It can be seen that this order (with one exception) is the order of an increased degree of sin-

TABLE 5  
CO ADSORPTION ON SINTERED Pd-CHARCOAL CATALYSTS

Catalyst		Heat treatment		From X-ray data		CO monolayer adsorption molecules × 10 <sup>19</sup> /g-cat.	Ratio Pd (exposed) CO (adsorbed) <sup>a</sup>
% Pd (nominal)	Type	(°C)	(hr)	Pd area <sup>a</sup> per g-Pd (m <sup>2</sup> )	Exposed No. Pd atoms <sup>a</sup> × 10 <sup>19</sup> /g-cat.		
5	B2	700	20	23	1.43	1.50	0.95
5	B2	800	20	17	1.12	0.99	1.13
10	C2	760	22	14	1.77	0.97	1.83
10	B2	900	70	9	1.24	0.57	2.18
20	A1	790	20	12	3.57	1.55	2.31
5	B2	900	66	10	0.65	0.22	2.96
Pd black		—	—	—	27.2	7.63	3.57

<sup>a</sup> Apparent Pd area and number of Pd atoms exposed, neglecting crystallite aggregation.

tering as indicated by the Pd area (from X-ray data) per unit weight of metal. The Pd/CO ratio for a Pd black (also reduced at 25°C, evacuated at 100°C before CO chemisorption) is included for comparison.

Values of the ratio, Pd (exposed)/CO (adsorbed), vary from unity to almost 3 for these sintered Pd-charcoal catalysts. Apart from the rather improbably higher ratios, it is *not* believed that the ratio changed in response to any crystallite size effect for the following reason: The distribution of different adsorption sites can vary markedly with crystallite size, but, as shown by van Hardeveld and van Montfoort (8), these variations are mainly confined to the size range below 70 Å, whereas the Pd/CO ratios in Table 5 refer to sintered catalysts with much larger crystallites. Hydrogen retained by the surface as a consequence of the low degassing temperature during the pretreatment might cause high Pd/CO ratios, but there is no reason why the amount should vary for the series of catalysts in Table 5. The Pd/CO ratio observed for the Pd black in Table 5, and especially the even higher Pd/CO ratios implied by results for other Pd blacks in Table 1, suggest an

alternative explanation. (Note: Ratios shown in Table 1, column 5, are X-ray intensity ratios; for Pd/CO ratios, divide results in column 4 by results in column 3.) It is believed that high Pd/CO ratios in sintered Pd-charcoal catalysts, i.e., Pd/CO ratios greater than unity, are caused by aggregation of Pd crystallites with attendant loss of exposed surface for CO chemisorption. In effect, Pd areas calculated from X-ray line-broadening will be too high when aggregation of the Pd crystallites occurs.

#### *High-dispersion Pd-Charcoal Catalysts*

Satisfactory CO adsorption isotherms were also obtained for Pd-charcoal catalysts which had not been deliberately sintered and still contained highly-dispersed Pd (Fig. 3). Again, the catalysts were reduced at 25°C and evacuated at 100°C before CO adsorption. Table 6 shows the volumes of CO adsorbed and X-ray data (fraction Pd detected, crystallite size) obtained from the actual samples *after CO adsorption measurement*.

In these catalysts, much of the Pd is effectively 'X-ray amorphous', i.e., present as crystallites <50 Å size which predominantly determined the total Pd area. In

TABLE 6  
CO ADSORPTION ON HIGH DISPERSION Pd-CHARCOAL CATALYSTS

Catalyst		X-ray data			Size (Å) of undetected crystallites for Pd (exposed)/CO (adsorbed) ratios			
% Pd (nominal)	Type	Fraction detected	Crystallite size (Å) of detected Pd	CO monolayer adsorption ml/g-cat.	Overall <sup>a</sup> mean size (Å)	= 1.0	= 1.5	= 2.0
5	C1	0.37	60	2.68	35	28	17	12
5	A1	0.51	180	2.31	45	25	16	12
10	A1	0.32	130	4.56	35	26	17	13
10	A2	0.50	115	5.22	37	22	14	10
20	A1	0.66	125	7.48	50	24	14	10
						25 (mean)		
1	B1	0.26	170	0.38	50	40	26	19
1	B2	0.27	210	0.40	52	38	24	20
5	B1	0.17	145	2.35	43	39	25	19
5	B1	0.52	100	1.55	63	45	26	18
10	B2	0.38	110	3.34	57	44	27	20
						26 (mean)		

<sup>a</sup> Overall mean crystallite size from CO adsorption, assuming Pd (exposed)/CO (adsorbed) ratio = 1.

these circumstances, any assumptions about the mean size of crystallites <50 Å size have a large effect on Pd areas calculated from X-ray data. Therefore, the Pd (exposed)/CO (adsorbed) ratio cannot be directly estimated, and the following approach has been adopted.

Experiments with sintered Pd-charcoal catalysts, as described above, gave some support for the view that a Pd/CO ratio of unity might be used. (Observed values greater than unity were ascribed to crystallite aggregation.) However, a variety of Pd/CO ratios might be deduced from other studies, e.g., infrared, LEED etc., and therefore, in Table 6, ratios of 1.0, 1.5, and 2.0 have been assumed, and the corresponding mean size of the 'X-ray amorphous' Pd fraction calculated from data in columns 3-5. Thus in the first group of catalysts, (types C1 and A1), if the Pd/CO ratio is unity, then the mean size of the 'X-ray amorphous' fraction is 25 Å. In the second group of catalysts (type B1), the Pd/CO ratio has to be 1.5 if the mean size of the 'X-ray amorphous' fraction is again to equal 25 Å.

Alternatively, the Pd (exposed)/CO (adsorbed) ratio may be, for example, unity for both groups of catalysts, but the crystallite size distribution may cut off sharply in type B1 catalysts, so that in this second group of catalysts, the mean size of the 'X-ray amorphous' fraction is indeed ~40 Å. This, however, seems unlikely.

A direct test of the Pd/CO ratio, using electron micrographs, is not readily accomplished, because only crystallites in small areas of the micrographs can be sized, due to the effort involved. Furthermore, the electron micrograph chosen is itself a subjective impression of what constitutes a typical view of the sections examined, and these sections represent only a minute fraction of the catalyst prepared.

With these reservations, an electron micrograph (Fig. 4a) and the corresponding histogram (Fig. 4b), showing the crystallite size distribution in a 1% Pd-charcoal catalyst (type B2), are presented. The

crystallites were sized in terms of their diameters, as they appear approximately spherical, in increments of 10 Å.

From this information, different kinds of average diameter can be derived. It might be noted that in the tables, average diameters based on X-ray crystallite sizes were used in making comparisons involving surface area, which is not strictly correct. Again, the data from electron microscopy on numbers and sizes of crystallites will be used to derive the kind of average diameter available by X-ray measurements. It has been commonly accepted that this represents a volume-weighted mean size  $\delta$  given by

$$\delta = \sum_i N_i \delta_i^3 / \sum_i N_i \delta_i^2, \quad (4)$$

where there are  $N_i$  crystallites of volume  $\delta_i^3$ , i.e., the X-ray diffraction crystallite size is interpreted as the cube root of the volume. For spherical crystallites of diameter  $d_i$ ,

$$\delta_i = [\pi/6]^{1/3} d_i, \quad (5)$$

or

$$\delta = [\pi/6]^{1/3} \bar{d} = 0.806 \bar{d}, \quad (6)$$

where

$$\bar{d} = \sum_i N_i d_i^3 / \sum_i N_i d_i^2, \quad (7)$$

to be determined from the electron micrograph. For crystallites below 50 Å in the histogram,  $\delta = 26$  Å. Setting a lower X-ray detection limit than 50 Å can only decrease this value. Therefore, within the limitations mentioned above, electron microscopy supports the view that the mean crystallite size of the 'X-ray amorphous' fraction in a type B1 is ~25 Å, and hence for these type B1 catalysts, the Pd (exposed)/CO (adsorbed) ratio could be 1.5 (cf. Table 6). For sintered catalysts (Table 5), in the absence of aggregation, and for unsintered type C1 and A1 catalysts (Table 6), the evidence possibly indicates a Pd/CO ratio of 1.0.

The infrared spectrum of CO adsorbed on silica-supported Pd often shows two regions of absorption, near 4.8  $\mu\text{m}$  and 5.2  $\mu\text{m}$ , assigned to the C-O stretching

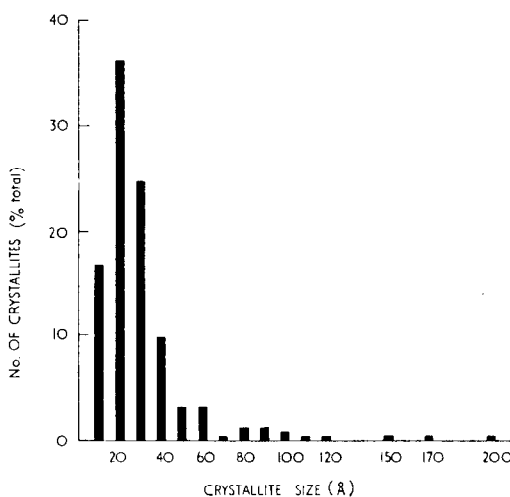


FIG. 4. (a) Electron micrograph from ultramicrotome section of (nominal) 1% Pd-charcoal catalyst, type B2, after CO adsorption measurement, with magnification, 100,000 $\times$ . (b) Size distribution of Pd crystallites in (part) of Fig. 4a.

mode of 'linear' and 'bridged' species (9), respectively; the latter species is enhanced by the presence of large crystallites (10). Unfortunately such observations cannot

now be translated into Pd (exposed)/CO (adsorbed) ratios while doubt exists about the necessity of considering both linear and bridged species to explain the infrared

results (11). While LEED results refer to extended single-crystal surfaces of major planes, they do indicate the complexity of CO adsorption on metal surfaces. On the Pd (100) surface, at exactly 0.5 monolayer coverage, a  $c(4 \times 2) - 45^\circ$  overlayer structure forms, which is in complete registry with the substrate, but at coverages  $>0.5$ , the structure is uniaxially compressed, and CO molecules are no longer localized on sites of high coordination with the substrate (12). Thus larger numbers of CO molecules are packed on to the Pd (100) substrate than might have been expected (13), and consequently, the ratio Pd atoms (exposed)/CO molecules (adsorbed) can be substantially less than 2.

### CONCLUSIONS

The measurement of metal dispersion or area is difficult for practical Pd-charcoal catalysts, because any vigorous attempts to reduce or outgas the catalyst before chemisorption may induce extensive sintering. X-Ray diffraction is particularly useful in these circumstances, because surface cleaning is avoided, but the determination of crystallite size from line-broadening must be supplemented by intensity measurements, so that the amount of 'X-ray amorphous' (highly dispersed) palladium can be estimated.

Using this information from X-ray diffraction, it was found that even the mildest surface cleaning ( $H_2$  at  $25^\circ C$ ; evacuation at  $100^\circ C$ ) can induce sintering. However, the extent of sintering is small at low palladium contents and also minimized by a uniform palladium distribution over the charcoal support.

Although only a mild surface cleaning treatment was applied, nevertheless the amounts of CO chemisorbed were sensible (in relation to X-ray-electron microscope

information) and low Pd (exposed)/CO (adsorbed) ratios were obtained. If it can be shown for a given type of Pd-charcoal catalyst, using these physical techniques, that sintering is not excessive for the surface cleaning condition specified in this work, then CO chemisorption measurements can be used on a routine basis for Pd area determination. In these circumstances, the areas measured by CO chemisorption would be a good indication of the actual Pd area of the 'as prepared' catalyst.

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