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Characterization of Palladium Blacks

II. Comparison of Various Methods for Estimating Surface Area or Particle Size

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Series of palladium blacks of widely differing surface area have been characterized by techniques including nitrogen and krypton adsorption, hydrogen chemisorption, electron microscopy, and X-ray diffraction. The precision of these techniques is estimated from a comparison of the results obtained.

INTRODUCTION

Prior to a study of the effect of the surface area of a palladium black upon its sorption of gaseous hydrogen (*1*), the series of palladium blacks employed were characterized. The techniques used and the results obtained are described in this paper.

EXPERIMENTAL METHODS

Materials. The palladium blacks used were those specified in Part I (*2*). Ultrapure hydrogen was prepared as indicated in Part I (*2*). Grade X helium, nitrogen, and krypton were obtained from British Oxygen Co. Ltd.

Nitrogen and krypton adsorption. Measurements were carried out in precision BET volumetric apparatus at −196°C. The data obtained for samples pre-adsorbed with oxygen were plotted according to the BET equation and gave good reversible straight lines in the range $0.03 < p/p_0 < 0.30$ with saturation vapor pressure p_0 taken as 253 N m^{-2} (0.19 cmHg) for krypton and in the range $0.04 < p/p_0 < 0.24$ for nitrogen. The values of the constant c were always >100 and so the values chosen for p_0 did not greatly affect the surface areas determined. The molecular cross-sectional areas for nitrogen and krypton were taken as 0.162 and 0.202 $(nm)^2$ (*3*).

Hydrogen chemisorption. Both the technique of hydrogen chemisorption and the apparatus used are fully described in Part I (*2*).

Electron microscopy. Electron micrographs of the palladium samples were obtained using a transmission electron microscope (Hitachi HU 11B). The samples were found to consist of aggregates of basic particles, and these were dispersed in dilute sodium hexametaphosphate by means of an ultrasonic probe. The specimens were replicated using carbon, the palladium was removed by floating the replicas on concentrated HNO_3 and shadowed with either platinum or chromium. Particle size counts were carried out on several electron micrographs of each sample using a Carl Zeiss instrument type TGZ 3.

X-ray diffraction. The diffraction patterns of the palladium blacks, obtained by both diffractometer and camera techniques, exhibited line broadening, which limited the accuracy with which the lattice parameters could be determined.

The observed line breadths at half-maximum intensity were corrected for experimentally measured instrumental broad-

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ening, by Warren's method, and for $K\alpha$ doublet broadening to give the intrinsic line breadths B (*4*). When X-ray line broadening can be attributed solely to crystallite size effects, the relationship $B = B_c = K_1\lambda/t\cos\theta$, where B_c is the crystallite size line broadening, K_1 is a constant called the shape factor [taken as 0.893 (*4*)], λ is the wave length, t is the apparent crystallite size in the range 5 to 100 nm and assumed to be the cube root of the crystallite volume, and θ is the Bragg angle, can be used for the determination of crystallite sizes (*5*). If, however, other line broadening effects, such as strain, are also present, this relationship leads to crystallite sizes that are too low. Strain line broadening B_s is given by $B_s = K_2\tan\theta$, where K_2 is a constant and is proportional to the strain of the sample (*6*). Assuming Cauchy line profiles, the crystallite size and strain line breadths are additive (*6*), $B = K_1\lambda/t\cos\theta + K_2\tan\theta$, and t could be determined from the intercept of a linear plot of $B\cos\theta$ versus $\sin\theta$ (*7*). Unfortunately the line breadths from different effects are not exactly additive and the gradient K_2 will vary with θ if the strain is non isotropic. However this summation was found to be more satisfactory than that assuming that the line profiles were Gaussian and that $B^2 = B_c^2 + B_s^2$ (*6*), and deviations from linearity were small. To convert the value of t obtained to an average crystallite size D_{av}, the shape of the crystallites must be assumed. For spherical crystallites $t = 0.806 \times D_{av}$ (*5*), where D_{av} is the average crystallite diameter, and for cubic crystallites $t = D_{av}$, where D_{av} is the average crystallite edge. Thus for a sample consisting of a mixture of such crystallites $t \leqslant D_{av} \leqslant t/0.806$.

RESULTS

The surface areas determined by the nitrogen and krypton adsorption and hydrogen chemisorption techniques are given in Table 1.

Figures 1a,b and 2 illustrate the results obtained by electron microscopy for the samples A, B, C, and E. All electron micrographs obtained indicated that the samples consisted of aggregates of basic particles. Direct electron microscopy showed that with increasing surface area there was a trend from large well-defined particles (Fig. 1a) to smaller spherical particles (Fig. 1b). The replica electron micrographs indicated the extent of aggregation of particles in the samples (Fig. 2). Particle size counts on over 1000 particles were made from the electron micrographs of each sample and the volume weighted average particle size, given by $(\Sigma N_iD_i^4/\Sigma N_iD_i^3)$ (*5*) where N_i is the number of particles of size D_i, was calculated and given in Table 1 for each sample.

The extrapolation technique was used to correct the X-ray intrinsic line broadening

TABLE 1
CHARACTERIZATION DATA FOR PALLADIUM BLACKS

	Sample	A	B	C	D	E
Surface area/m²g⁻¹	Nitrogen BET			31.3_0		
	Krypton BET 1	3.5_4	7.1_5	30.8_1		66.0_7
	2	3.4_3	7.1_6	30.6_4		64.7_8
	Hydrogen Chemisorption 1	3.6_3	7.4_1	32.7_0	66.2_9	71.8_6
	2					68.0_3
	3					71.7_1
	Av surface area	3.5_3	7.2_4	31.3_6	66.2_9	68.4_9
Particle or crystallite size/nm	Electron microscopy	113	70	16		7
	X-ray (spherical particles)	109	29	19	12	11
	(cubic particles)	88	23	15	10	9
	Calc from av surface area assuming discrete uniform particles	141	69	16	8	7

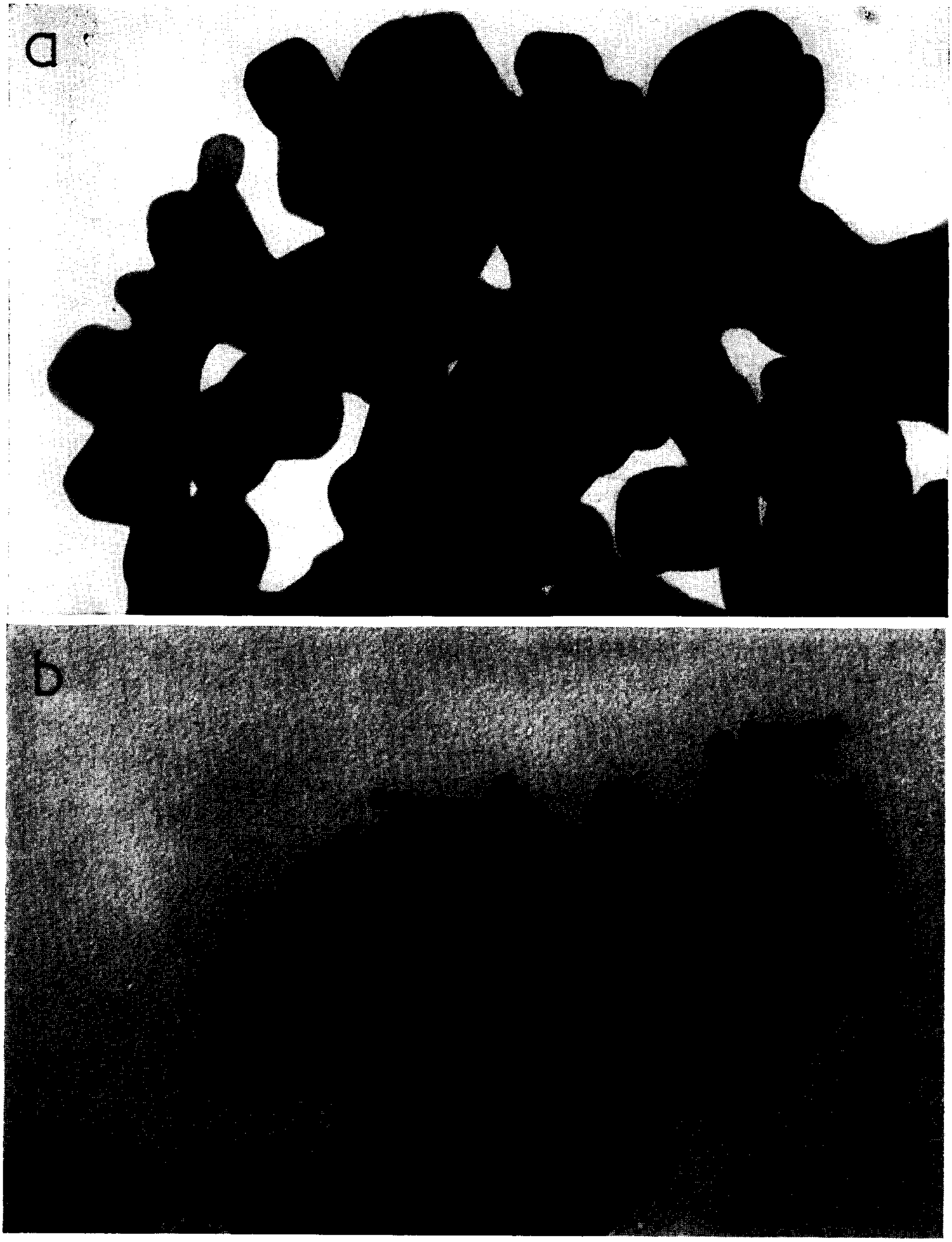

FIG. 1. Direct transmission electron micrographs of: (a) palladium black A (× 272,000); and (b) palladium black E (× 482,000).

for the effects of strain and the values of apparent crystallite size for each sample were converted to average crystallite sizes which are given in Table 1.

An average particle size can be calculated from the average surface area S_{av} assuming that the sample consists of uniform discrete particles, since

FIG. 2. Electron micrograph of platinum shadowed carbon replica of palladium black B (× 113,000).

$$\frac{D_{\text{calc}}}{(\text{nm})} = \frac{6 \times 10^3}{\dfrac{\rho}{(\text{g cm}^{-3})} \cdot \dfrac{S_{\text{av}}}{(\text{m}^2\,\text{g}^{-1})}}$$

where ρ is the density and D_{calc} is the average calculated edge for a sample of cubic particles, or is the average calculated diameter for a sample of spherical particles. The particle sizes so calculated for each sample are given in Table 1.

CONCLUSION

The agreement between the surface area data measured by BET and hydrogen chemisorption techniques is good, and the data obtained for each sample was always within 2–5% of the average area. This indicates the validity of the hydrogen chemisorption technique (*2*).

Both of the methods of particle size/crystallite size determination used involve some uncertainties. In taking particle size counts from electron micrographs, there is always the problem of whether the count is truly representative of the sample. This is particularly true for the present samples, where the aggregation obscures many particles at the center of the aggregates even when using the replica technique. The X-ray line broadening method not only involves uncertainties as to the validity of the method of summation and the isotropy of the strain, but also requires the assumption of crystallite shapes. Table 1 shows that for these samples the terms particle size and crystallite size are synonymous. The particle sizes derived from electron microscopy agree very well with those calculated from the average surface areas. However, the agreement between crystallite sizes measured from X-ray line broadening and particle sizes calculated from the average surface areas is not as good and is better when the crystallites are assumed spherical at low surface area and cubic at high surface area. This is the opposite of the particle shapes revealed by electron microscopy.

Both nitrogen and krypton adsorption and hydrogen chemisorption techniques provide precise and reproducible surface areas of palladium blacks. Electron microscopy can yield valuable information on particle shapes and aggregation and also average particle sizes of high accuracy from counts of a suitable number of particles. X-ray diffraction line broadening of palladium samples exhibiting strain and crystallite size line broadening can lead to no more than an approximate estimate of crystallite size without more rigorous analysis and a greater knowledge of sample crystallite shapes.

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