PLATINUM CATALYSTS SUPPORTED ON GRAPHITIZED CARBON BLACK—II

CHARACTERIZATION OF THE PLATINUM BY SMALL ANGLE X-RAY SCATTERING AND TRANSMISSION ELECTRON MICROSCOPY

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Abstract—Particle sizes of platinum dispersed on a graphitized carbon black (Vulcan 3G) and samples resulting from its prior oxidation in air at 798 K have been measured by Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM). Mean diameters of platinum particles decrease with increasing burn-off of the carbonaceous supports. The values of mean diameters as determined by these physical methods agree well with those estimated from gas titration procedures. Size distributions of the platinum particles are also described in terms of log-normal functions.

1. INTRODUCTION

In the initial paper in this series[1], gas titration and differential calorimetric methods were used to characterize a group of platinum catalysts supported on graphitized carbon black. As was concluded in that contribution, the chemisorptive methods are somewhat fraught with difficulties because of problems in ascribing unique or consistent stoichiometries. In addition, these procedures yield information on the average size of dispersed catalyst and do not describe size distributions. It was decided, therefore, to characterize further these catalysts by physical methods in an attempt to determine size distributions for the supported platinum. The methods selected were Small Angle X-ray Scattering (SAXS) and Transmission Electron Microscopy (TEM); both of which have previously met with success in characterizing supported catalysts[2–6].

2. EXPERIMENTAL

Preparation of the catalysts has been described in the preceding paper[1]. It will be recalled that they all contained about 1% platinum by weight. The supports were a graphitized carbon black (V3G) and four samples of V3G which had been activated to differing levels of carbon burn-off.

2.1 *SAXS studies*

The catalysts are composed of three phases, each with a distinctive electron density, i.e. platinum, carbon and air. Consequently, a study by SAXS directly on these materials would be difficult to interpret[7]. Thus, an experimental approach described by Whyte *et al.*[2] for platinum dispersed on alumina was adapted for this study. In this procedure, interparticulate spaces within the support (i.e. air) are filled with a liquid of electron density similar to that of the support. In this manner, the overall system behaves as though it is composed of only two phases—platinum and support. Several liquids were tested as maskants. It was found that bromobenzene met the experimental requirements best in terms of its electron density and absorptivity. A small quantity of the catalyst (previously reduced in H_2 at 723 K) was mixed thoroughly with an amount of bromobenzene sufficient to ensure complete wetting. It was noted, however, that excess liquid caused poor reproducibility. The bromobenzene/catalyst mixtures were then placed in 1.5 mm thin-walled quartz tubes prior to examination by SAXS.

All SAXS measurements were made with a Kratky camera with a specimen to exit slit distance of 214 mm. Scattered X-radiation was scanned from approximately 0.12 to 1.0° (2θ). Monochromatization of Cu Kα radiation was achieved by use of Ni filters and a peak height analyzer. Detection was made by a scintillation counter. Experimentally derived SAXS intensity curves were corrected for background and deviations from Porod's law[8].

The size distribution calculated from the SAXS data is expressed in terms of log-normal functions; the validity of this assumption was tested by examination by TEM and is discussed later. Granqvist and Buhrman[9] indicate that supported metal catalysts tend to follow log-normal size distributions. However, Ehrburger and Walker[5], from TEM data, show that for catalysts similar to those used in this study, this distribution function is not always obeyed.

Whyte *et al.*[2] and Neilson[10] have shown that log-normal distributions can be generated from SAXS data if two characteristic radii for the scattering units can be defined. Following the method described by these authors[2, 10], the radii selected are the Guinier spherical

radius of gyration, R_E, and a Porod spherical radius, R_p. It can be shown that these radii can be defined by different moments of the spherical radius, R, by:

$$R_E^2 = \frac{\langle R^7 \rangle}{\langle R^5 \rangle} \quad \text{and} \quad R_p = \frac{\langle R^3 \rangle}{\langle R^2 \rangle}. \tag{1}$$

The spherical radius of gyration, R_E, was determined from the linear portion of a plot of $\ln J(h)$ vs h^2 using the Guinier approximation[11], i.e.

$$\ln J(h) = \ln J_0 - h^2 R_E^2/5 \tag{2}$$

where $J(h) =$ scattered intensity† at a scattering angle defined by h; $h = 2\pi \sin 2\theta/\lambda$, $2\theta =$ scattering angle, $\lambda =$ X-ray wavelength; and J_0 is the extrapolated intensity at zero angle.

The Porod radius was experimentally derived from [12];

$$R_p = \frac{3\pi a}{16(1-c)} \tag{3}$$

where $c =$ volume fraction of the scattering centers; $a =$ the correlation distance which was determined from the Debye–Williams approximation[13–15].

The log-normal distribution $F(R)$ takes the form (in terms of radius, R)

$$F(R) = \frac{1}{R \ln \sigma \sqrt{\pi}} \exp - \left[\frac{(\ln R - \ln \mu)^2}{2 \ln^2 \sigma} \right] \tag{4}$$

where $\mu =$ geometric mean of the distribution and $\sigma =$ geometric standard deviation of the variance. From considerations of the various moments of R, it is possible to derive the following equations for μ and σ in terms of the experimentally determined radii R_E and R_p.

$$\ln \mu = \ln R_E - 1.71 \ln(R_E/R_p) \tag{5}$$

$$\ln^2 \sigma = 0.286 \ln(R_E/R_p) \tag{6}$$

Finally, from the log-normal function an average radius (R_s) on a number surface basis can be estimated from [16]:

$$R_s = \exp(\ln \mu + \ln^2 \sigma) \tag{7}$$

and, thus, an average diameter on the same basis is given by

$$2R_s = \bar{D}_s. \tag{8}$$

2.2 TEM studies

Electron microscopy studies of the catalysts were conducted using a Philips EM-300 TEM operated at 100 kV. Samples were dispersed ultrasonically in toluene. A few drops of the suspension were spread over self-perforated microgrids[17]. Direct magnification was
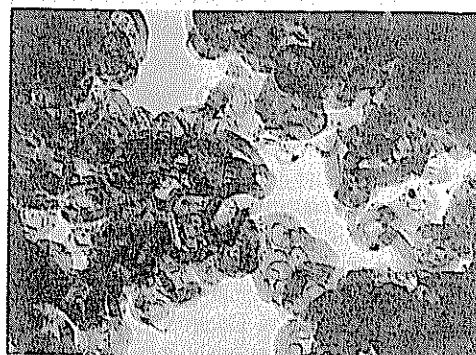
† This equation is derived for slit-smeared intensity data [i.e. $J(h)$] such as obtained by use of a Kratky camera.

10^5X, and platinum particles were measured at a final magnification of 4×10^5X. Under these experimental conditions, the smallest range of detectable particles was fixed between 0 and 2 nm. Higher size intervals were fixed at 1 nm. In order to attain statistically significant data at least 2000 particles of platinum were measured for each catalyst. In each case, the surface mean diameter, $\bar{D}_{sm}$, and the arithmetic mean diameter, D_a, were calculated from;

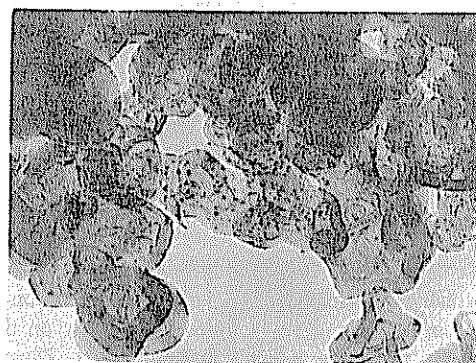$$\bar{D}_{sm} = \sum n_i d_i^3 \bigg/ \sum n_i d_i^2 \tag{9}$$

$$D_a = \sum n_i d_i \bigg/ \sum n_i. \tag{10}$$

(a)

(b)

(c)

Fig. 1. Electron microscopy micrographs of some catalysts (1,100,000 X): (a) V3G-0; (b) V3G-24.6; (c) V3G-74.2.

3. RESULTS AND DISCUSSION

In order to validate the assumption of log-normal behavior, one must first examine the results of the TEM study. Figure 1 shows typical TEM micrographs obtained for these materials. It can be seen that they indicate the presence of platinum particles which are well dispersed and essentially spherical. Detailed analysis of the micrographs yields histograms (Fig. 2) in which the percentages of the total number of particles are plotted vs particle diameter. The broadest distributions are noted for platinum particles on V3G-0 and V3G-9.3 supports. However, activation of the support produces an increased population of platinum particles of less than 2 nm dia. This trend becomes more evident as the level of prior carbon activation increases; approximately 80% of the counted platinum particles on V3G-74.2 have diameters less than 2 nm. Additionally, platinum distributions appear to be narrower for the highly activated supports. These results are somewhat different to those reported by Ehrburger and Walker[5]. They found that the platinum distribution on activated V3G was very narrow; over 90% of the catalyst particles on a sample similar to V3G-24.6 were less than 2 nm in diameter.

However, Ehrburger and Walker used a different procedure to activate the V3G than that used in the present study. That is, they followed activation in air at 773 K with additional activation by treatment with concentrated nitric acid for 24 hr at reflux temperature.

Table 1 lists the values of mean diameters calculated from examination of the TEM micrographs. These data reveal, again, that as the burn-off of the support increased, the average size of catalyst particles decreased.

Figure 3 presents log probability plots for platinum particles on the supports as determined by TEM. This figure indicates that the platinum size distributions for all samples can be fitted to a reasonable degree to log-normal probability functions.

Experimentally determined values of R_E and R_p from SAXS measurements are also given in Table 1. These data were used to calculate the log-normal distribution functions; geometric mean radii (μ) and the surface mean diameters ($\tilde{D}_s$) show good agreement with $\tilde{D}_{sm}$ obtained by TEM.

Figure 4 is a plot of $F(R)$, i.e. radius log-normal distribution functions, for each of the catalysts as determined from the SAXS data. From these plots, it can be seen that V3G-0 has the broadest distribution of platinum sizes; confirming the TEM observations (Fig. 2). Again, as the degree of prior activation of the support increases, the distributions narrow because of the in-
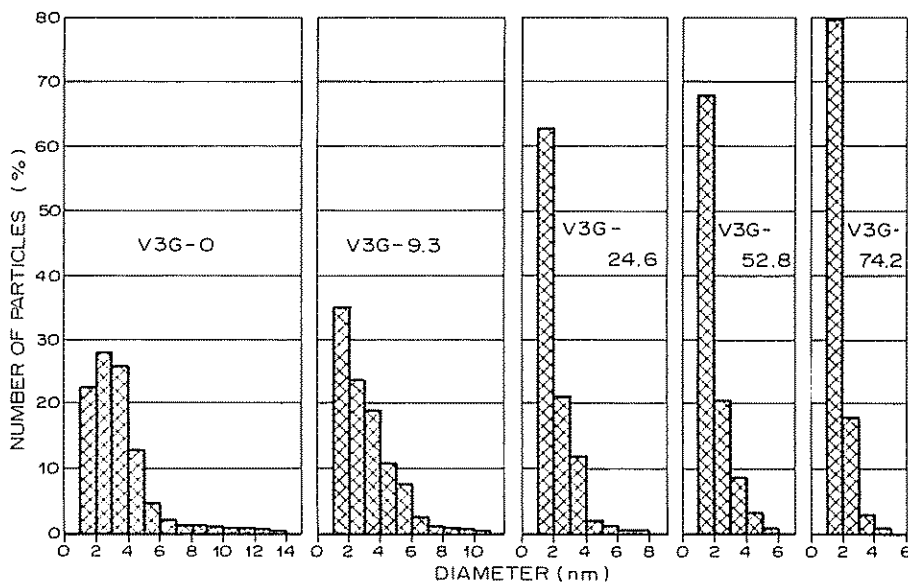

Fig. 2. Particle size histograms (electron microscopy).

Table 1. Mean dimensions for supported platinum from TEM and SAXS measurements

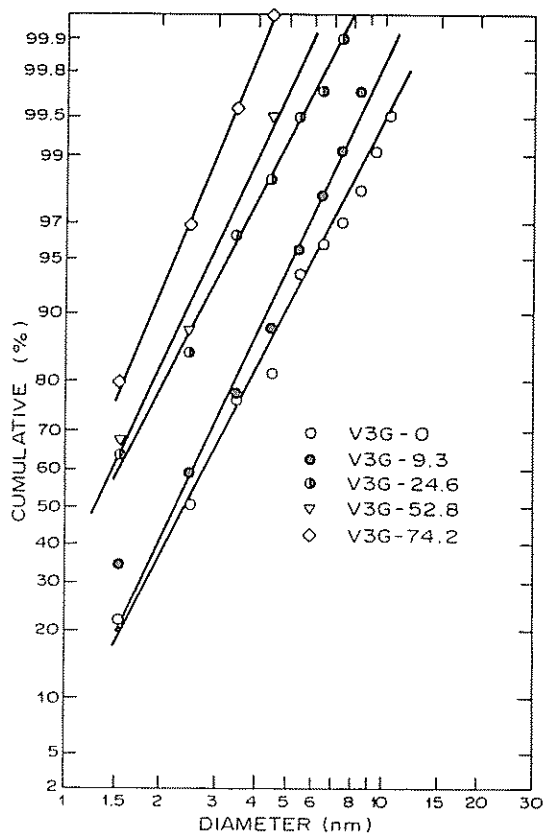| Catalyst	SAXS Size Parameters (nm)				TEM Diameters (nm)	
	R_E	R_p	μ	$\tilde{D}_s$	D_a	$\tilde{D}_{sm}$
V3G-0	13.6	4.4	1.9	5.4	3.3	5.5
V3G-9.3	10.2	3.3	1.5	4.1	3.0	4.8
V3G-24.6	9.7	3.1	1.4	3.8	2.1	3.2
V3G-52.8	9.2	2.8	1.2	3.4	2.0	2.8
V3G-74.2	8.0	2.4	1.0	2.8	1.7	2.1

Fig. 3. Log probability plots of platinum particles.

creased populations of small platinum particles. It has been suggested in the preceding paper[1] that the observed increase of platinum dispersion with increasing level of activation of the support is principally influenced by accompanying increases in support surface area.

Before making comparisons between these physical methods and the chemisorptive procedures[1] one must first examine the limitations of TEM and SAXS. Dealing first with TEM, it has been shown by Yacaman and Dominguez[18] that this technique can underestimate the number of small particles. Thus, this procedure will tend to yield distributions biased toward larger particles unless special precautions are taken. In addition, Ehrburger and Walker[5] have discussed potential problems encountered in estimating the contributions of the smaller particles. Secondly, the procedure selected in this study for generating log-normal size distributions from SAXS data are highly dependent on absolute values of the two characteristic radii, R_E and R_p. Each of these radii are, by themselves, weighted averages. Most significantly, R_E will be weighted toward larger particles and, thus, the resulting distributions will be biased in favor of larger scattering entities.

In Table 2 a comparison is made of the physically derived mean diameters, $\bar{D}_{sm}$ and $\bar{D}_s$, with those calculated from gas titrations described previously[1]. The Pt/O ratio of "1 or 2" listed for a O_2/CO titration refers to the fact that two of the stoichiometries considered (eqns 11 and 12[1]) will yield the same results in terms of CO consumed per platinum site although their Pt/O
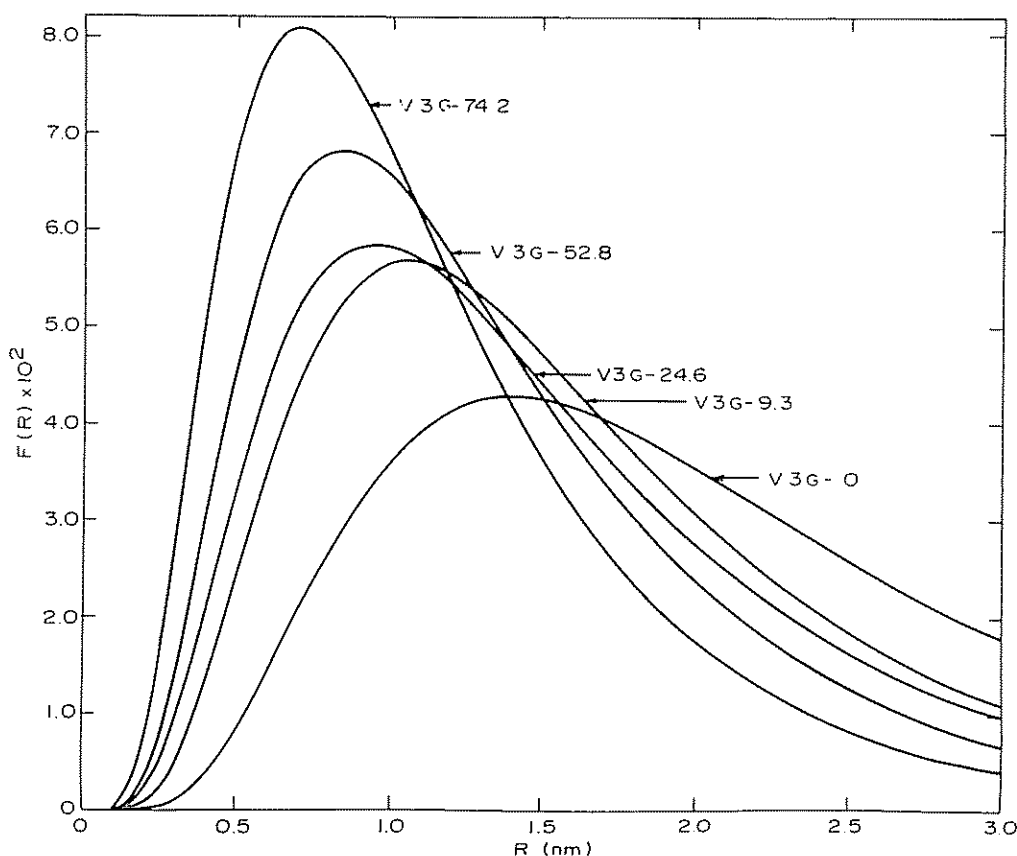

Fig. 4. Log-normal distributions determined by SAXS.

Table 2. Mean diameters of platinum particles from titrations (1), SAXS and TEM

	Pt/O ratio →	Mean Diameters (nm)							SAXS/TEM	
		Titration Reaction								
		O_2/H_2		H_2/O_2		O_2/CO				
Catalyst		1	2	1	2	1	1 or 2	2	$\bar{n}_{sm}$	D_s
V3G-0		6.8	4.3	3.7	2.5	6.4	4.9	3.2	5.5	5.4
V3G-9.3		3.5	2.3	–	–	4.9	3.7	2.5	4.8	4.1
V3G-24.6		2.9	1.9	2.6	1.7	4.3	3.3	2.2	3.2	3.8
V3G-52.8		2.6	1.8	2.5	1.7	3.7	2.8	1.9	2.8	3.4
V3G-74.2		2.0	1.3	2.2	1.5	3.1	2.3	1.6	2.1	2.8

ratios differ. Inspection of Table 2 indicates that the two physical methods tend to favor the chemisorptive reaction schemes which are based on a Pt/O ratio of 1. This observation also agrees with the calorimetric data described previously[1]. It appears as though reaction schemes which utilize a Pt/O ratio of 2 tend to yield smaller diameters which agree less with those derived from TEM and SAXS. However, because of the aforementioned limitations in these physical techniques, these data cannot be considered as definite proof that one stoichiometry is better than another.

4. CONCLUSIONS

Both TEM and SAXS procedures can be successfully utilized to characterize platinum catalysts in terms of average particle size and size distribution. A combination of these physical techniques shows that the dispersion of platinum on graphitized carbon black supports is well described by log-normal functions. The results obtained confirm trends observed by chemisorptive titration procedures[1]; that is, the dispersion of platinum on these supports is primarily determined by the surface area of the support. In general, comparisons between data derived from TEM and SAXS with those obtained from gas titrations lend support for stoichiometries which incorporate a Pt/O ratio of 1. Finally, from this work and the previous paper[1], it is obvious that characterization of catalysts requires a multifaceted approach because no single method can adequately define their properties.

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