

## Carbon as a Support for Catalysts

### II. Size Distribution of Platinum Particles on Carbons of Different Heterogeneity before and after Sintering

P. EHRBURGER\* AND P. L. WALKER, JR.†

\**Centre de Recherches sur la Physico-Chimie des Surfaces Solides, 68200 Mulhouse, France,* and, †*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802*

Received February 22, 1978

The particle size of platinum dispersed on two carbon supports of different heterogeneity has been measured by electron microscopy. Differences in particle size distribution following sample preparation at 773 K on the two supports have been found. However, after sintering at 1020 K in argon for 48 hr a unique spectrum of size is reached by the metal particles independent of the heterogeneity of the carbon support.

#### INTRODUCTION

In a previous study, it has been shown that the specific surface area of platinum supported on carbon depends on the surface properties of the substrate (1). Thus by increasing the surface heterogeneity of the carbon, e.g., by gasification, it was found that the degree of dispersion of platinum particles increases considerably. Surface-area measurements of the platinum were performed by hydrogen chemisorption using the technique suggested by Benson and Boudart (2). Such a method yields only a mean value for the size of the platinum particles; it gives no information on their size distribution. Recently, attention has been drawn to direct measurements of particle size using electron microscopy (3-5). Although there is some uncertainty in the measurements of particles having diameters of less than 5 nm, these techniques may lead to new insights into the properties of supported catalysts. In particular, interactions of small solid particles

with substrates or sintering behaviors of the dispersed phase can be examined. The aim of the present study was to investigate the size distribution of platinum as a function of the surface properties of a carbon support. The sintering behavior of the supported platinum was examined by following the change in its size distribution.

#### EXPERIMENTAL METHODS

One of the carbon supports used was a graphitized furnace black Vulcan 3 (V3G), whose preparation was described earlier (1). The other support used was produced by the activation of the above support. Activation was performed in the following manner: gasification in dry air at 773 K to a burn-off of 21.4% by weight (1) and subsequent treatment with concentrated nitric acid for 24 hr at reflux temperature. The carbon was further washed and then dried at 420 K under vacuum (activated V3G).

Samples of platinum supported on the carbon substrates were prepared by the impregnation technique starting with chloroplatinic acid dissolved in a mixture of benzene and absolute ethanol. Reduction of the samples was carried out in flowing hydrogen for 10 hr at 773 K in a manner described earlier (1). Surface area measurements of the platinum were determined by hydrogen chemisorption as previously reported (1).

For sintering studies, the supported samples were heated in flowing argon (purity better than 99.995%) at 920 and 1020 K. The major impurities of the argon, as indicated by the manufacturer were  $N_2 < 40$  ppm,  $O_2 < 5$  ppm, and  $H_2O < 5$  ppm.

Supported samples were dispersed ultrasonically in toluene, and a few drops of the suspension were spread over self-perforated microgrids coated with an evaporated carbon film (5). Micrographs were taken with a JEOL JEM 100 B microscope operating at 100 kV and having a point-to-point resolution of 0.3 nm. Direct magnification was 100,000 $\times$ , and particles were measured at a final magnification of 500,000 $\times$ .

As discussed by Flynn *et al.* (6), several problems arise when measuring particle sizes below 5 nm. In order to avoid interference with the support film of the microgrid, only carbon black aggregates lying over a hole were taken into account. The size of such aggregates was typically in the range of 200 to 500 nm. The total change in defocus of a selected area is thus estimated below 300 nm. Flynn *et al.* (6) also showed that the apparent size of platinum particles on alumina may vary up to 1 nm depending on the defocus. In particular, sizes below 2 nm are affected by the defocus change. Thus, in our case, the lowest range of detectable particles was fixed between 0 and 2 nm, the following intervals being fixed at 1 nm. In order to obtain statistical significance, 2000 metal particles were measured for each sample. Below 4 nm, the

TABLE I  
Specific Surface Areas of Carbon Substrates and Supported Platinum (1% Loading)

| Substrate       | Surface area (m <sup>2</sup> /g) |          |
|-----------------|----------------------------------|----------|
|                 | Carbon                           | Platinum |
| Unactivated V3G | 56                               | 41       |
| Activated V3G   | 92                               | 160      |

particle diameters are known with a maximum uncertainty of  $\pm 0.5$  nm.

## RESULTS

### *Unsintered Samples*

Surface areas of both V3G samples, as well as surface areas of platinum for 1% metal loading, are given in Table 1. It has been shown previously that extensive gasification (activation) of the carbon substrate, up to 50% burn-off, leads to specific areas for supported platinum as high as 145 m<sup>2</sup>/g (1). Partial gasification of the carbon substrate followed by wet oxidation also promotes a high ultimate dispersion of platinum on the substrate.

Figures 1 and 2 are typical micrographs of platinum particles on unactivated and activated V3G supports. The platinum particles appear equiaxed. It is also noted that at the high magnification used the graphitic layers of the carbon can be seen as a result of phase contrast.

The corresponding histograms are shown in Fig. 3, where the percentage of the total number of particles is plotted vs particle diameter. For the unactivated V3G support, the size distribution of platinum is broad, with a few particles having diameters up to 15 nm. The size distribution of platinum on the activated support, on the other hand, is narrow. In fact, more than 90% of the counted particles have a diameter less than 2 nm. For each case, the arithmetic mean diameter,  $d_a = \sum n_i d_i / \sum n_i$ , and the surface mean diameter,  $d_s = \sum n_i d_i^3 / \sum n_i d_i^2$ , have been calculated. Assuming the



FIG. 1. Micrograph of platinum particles on unactivated carbon support following preparation at 773 K ( $\times 800,000$ ).

particles to be spherical, the mean diameter,  $\bar{d}$ , calculated from the specific surface area of the platinum as measured by hydrogen chemisorption, can also be determined. Values of the different diameters are com-

pared in Table 2. There is a reasonable agreement between  $d_s$  and  $\bar{d}$  for platinum particles, considering the maximum uncertainty in the measurement of particle diameter.

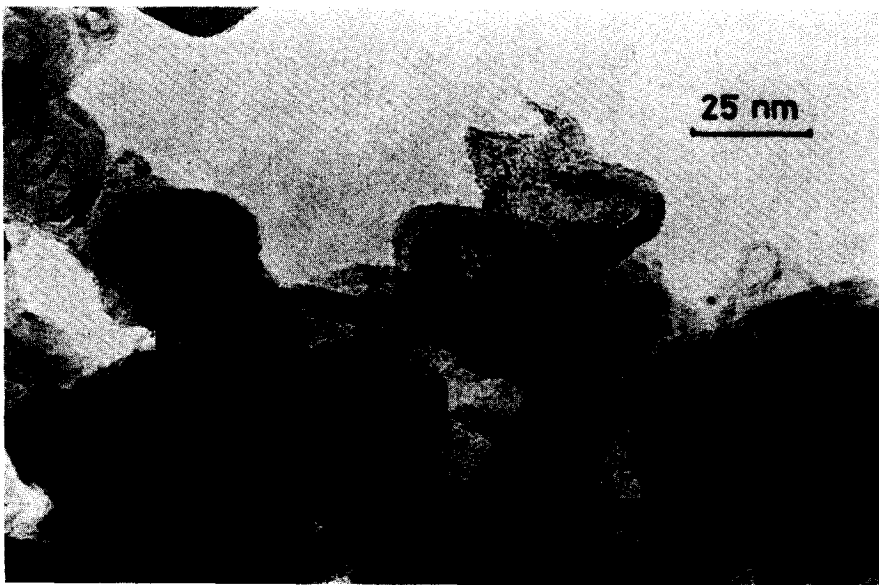


FIG. 2. Micrograph of platinum particles on activated carbon support following preparation at 773 K ( $\times 800,000$ ).

TABLE 2

Mean Diameters of Supported Platinum from Electron Microscopy and Chemisorption Measurements

| Substrate       | Diameters (nm) |       |           |
|-----------------|----------------|-------|-----------|
|                 | $d_n$          | $d_s$ | $\bar{d}$ |
| Unactivated V3G | 3.6            | 7.3   | 6.6       |
| Activated V3G   | 1.6            | 2.5   | 1.7       |

### Sintered Samples

Recently Granqvist and Buhrman (7) have shown that supported metal catalysts, like other finely dispersed systems, may follow a log-normal size distribution. Figure 4 presents log probability plots for platinum particles on the unactivated V3G support, both before and after heat treatment. Size distributions for all samples can be fitted satisfactorily to a log-normal probability function. Parameters of the log-normal distribution (geometric mean diameter  $d_g$  and geometric standard deviation  $\sigma_g$ ) were calculated using the relations for a sufficiently large number of particles:

$$\ln d_g = \sum n_i \ln d_i / \sum n_i$$

$$\ln \sigma_g = (\sum n_i [\ln(d_i/d_g)]^2 / \sum n_i)^{1/2}$$

Values of  $d_g$  and  $\sigma_g$ , compared to the mean arithmetic diameter, are given in Table 3. It is seen that in the case of the unactivated V3G support there is no significant change

in the platinum particle size distribution after heat treatment at 920 K for up to 48 hr. A slight coarsening of the metal particles is detected following heat treatment at 1020 K for 48 hr.

The behavior of the particles deposited on the activated V3G support upon heat treatment is strikingly different from the preceding behavior, as seen in Fig. 5 and Table 3. As already mentioned, more than 90% of the platinum particles on the unsintered sample are below 2 nm in size. Thus, it is only possible to ascertain the tail of the distribution. As mentioned above, the uncertainty of the measurement is about 0.5 nm, which limits considerably the accuracy of the determination of the distribution. However, it appears to be a form of "monodispersed distribution," most detectable particles having a diameter between 1 and 2 nm.

After heat treatment at 920 K, the percentage of particles below 2 nm sharply decreases, even for short treatment times. However, the platinum particles still cannot be described by a log-normal size distribution. Following heat treatment at 1020 K for 48 hr, the distribution of particle sizes can be fitted to a log-normal function. It is noteworthy to mention that at this stage, only 22% of the detected particles have a diameter less than 2 nm. Thus, on the oxidized support the initial particle size

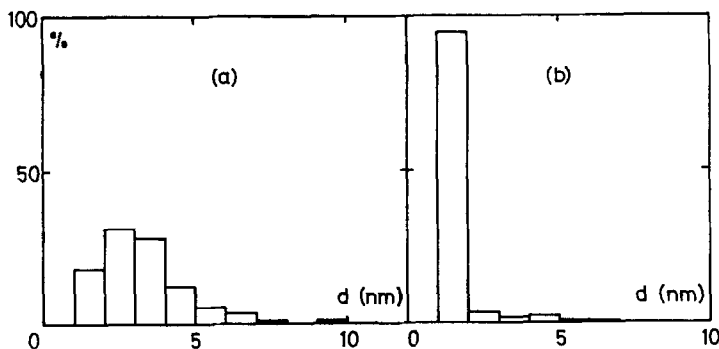


FIG. 3. Histograms of platinum particle size distribution following preparation at 773 K. (a) on unactivated support, (b) on activated support.

TABLE 3

Data for Platinum Particles Supported on Unactivated and Activated Carbon Substrates following Heat Treatment

| Heat treatment  | Unactivated support |            |            | Activated support |            |            |
|-----------------|---------------------|------------|------------|-------------------|------------|------------|
|                 | $d_{a,nm}$          | $d_{g,nm}$ | $\sigma_g$ | $d_{a,nm}$        | $d_{g,nm}$ | $\sigma_g$ |
| As prepared     | 3.6                 | 3.3        | 1.5        | 1.6               | —          | —          |
| 8 hr at 920 K   | 3.8                 | 3.3        | 1.6        | 2.0               | —          | —          |
| 24 hr at 920 K  | 4.0                 | 3.4        | 1.6        | 2.1               | —          | —          |
| 48 hr at 920 K  | 3.9                 | 3.3        | 1.7        | 2.3               | —          | —          |
| 8 hr at 1020 K  | 4.1                 | 3.4        | 1.8        | 2.3               | —          | —          |
| 48 hr at 1020 K | 4.5                 | 3.8        | 1.7        | 3.2               | 2.8        | 1.6        |

distribution is highly sensitive to heat treatment and tends, at higher temperatures, toward a log-normal distribution.

### DISCUSSION

#### Preparation of the Platinum Dispersion on Carbon

*Unactivated carbon support.* The fact that no change is observed for the platinum

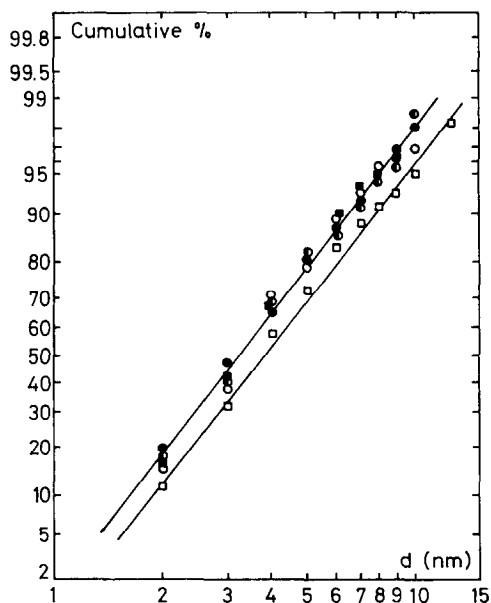


Fig. 4. Log probability plots of platinum particles on the unactivated carbon support as a function of heat treatment conditions. ●, as prepared; ●, 24 hr at 920 K; ○, 48 hr at 920 K; ■, 8 hr at 1020 K; □, 48 hr at 1020 K.

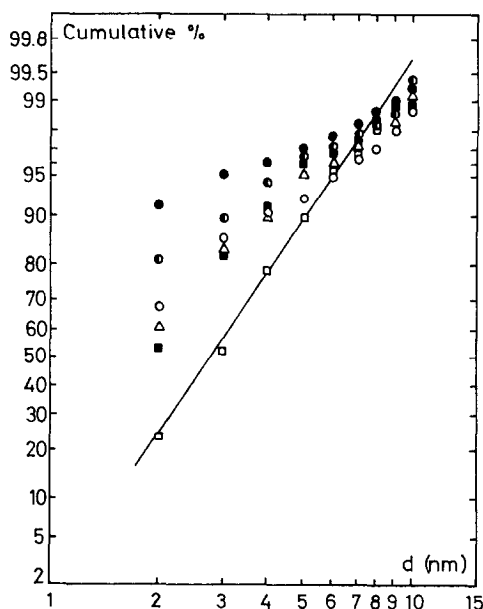


Fig. 5. Log probability plots of platinum particles on the activated carbon support as a function of heat treatment conditions. ●, as prepared; ●, 8 hr at 920 K; ○, 24 hr at 920 K; △, 48 hr at 920 K; ■, 8 hr at 1020 K; □, 48 hr at 1020 K.

particle size distribution on the unactivated carbon support in going from a preparation temperature of 773 K to a subsequent heat treatment temperature of 920 K indicates that the size distribution of platinum particles has been achieved at the lower temperature, presumably during the conversion of chloroplatinic acid to reduced platinum. The size distribution of the chloroplatinic acid aggregates on the carbon is unknown, but there are indications in the literature that the acid is generally well-dispersed on the substrate and that its coarsening occurs during heat treatment. In particular, Flynn and Wanke (8) have shown from electron microscopy studies of chloroplatinic acid deposited on alumina that agglomeration takes place during the reduction step. As discussed recently (9), there are two possible mechanisms for particle coarsening on a substrate: Particles move as a whole on the substrate and coalesce after binary collisions, or particles

grow by interparticle transport of single atoms or molecules (Ostwald Ripening). Granqvist and Buhrman (7) have concluded that log-normal distributions suggest a coalescence growth mechanism. Moreover, Prado and Lahaye (10) have shown that when carbon particles grow in the gas phase by coalescence, the particle size tends toward a log-normal distribution. Thus, on a homogeneous, low-energy graphitized carbon surface, the platinum species move on the substrate and coalesce during the reduction step, yielding at 773 K a log-normal particle size distribution.

*Activated carbon support.* In the previous paper, we discussed the expected increase in heterogeneities on the carbon surface as a result of its oxidation (1). Electron microscopy has shown that not only the mean diameter of the platinum particle size but also the width of the particle size distribution is affected when the carbon support becomes more heterogeneous. The enhanced dispersion of the platinum particles may result from the deposition of chloroplatinic acid in a more dispersed form and/or from a lower coarsening of the aggregates during their reduction. A lower coarsening could be a result of higher interaction of the particles with the carbon support and, thus, reduced mobility. Whatever the predominant factor, the important point is that after reduction at 773 K the platinum particle size distribution is rather monodisperse which would indicate that the aggregates of platinum species are more tightly held on the heterogeneous substrate than on the homogeneous substrate.

#### *Sintering Behavior of the Platinum Particles*

After heat treatment of both samples under sufficiently rigorous conditions, the platinum particles showed log-normal distributions, which suggests that the growth of the particles occurred mainly by particle diffusion and coalescence. Wong *et al.* (11) recently provided new information for the

growth mechanism of platinum particles supported on single crystal graphite. In particular, they showed by electron microscopy that at 1100 K and at a residual pressure of  $1.1 \times 10^{-5}$  Pa, sintering occurs by migration of platinum atoms from small particles to larger ones. In contrast, in the presence of O<sub>2</sub> at a pressure of  $1.3 \times 10^{-4}$  Pa, they observed motion of platinum particles on the substrate. Oxidation and etching of the graphite substrate was also observed under these conditions. This suggests two possible explanations for the enhanced particle mobility: (i) additional energy imparted to the particles as a result of the exothermicity of the carbon-oxygen reaction and (ii) reduced interaction of the particles with active carbon sites because of oxygen chemisorption on these sites (12). In this study, sintering was performed in a stream of Ar containing less than 5 ppm of O<sub>2</sub>. The partial pressure of the O<sub>2</sub> impurity could still have been as high as 0.5 Pa, which was greater than the O<sub>2</sub> pressure in the study of Wong *et al.* where motion of particles was observed.

Since during sintering the total volume of the dispersed phase remains constant, it is interesting to examine the change in the volume distribution of the particles. Ruckenstein and Pulvermacher (13) established that under diffusion-controlled conditions, the particle size distribution can be represented by a unique spectrum after sintering at high temperature. Taking the formalism of Swift and Friedlander (14) who first derived these equations, we have plotted in a similar way the ratio  $n_v/n_t$  vs  $\eta = v_i n_t / \Phi$ , where:

$n_v$  = number of particles per unit surface area of support having a volume larger than  $v_i$ ;

$n_t$  = total number of particles per unit surface area of support;

$v_i$  = volume range considered; and

$\Phi$  = total volume of metal per unit surface area of support.

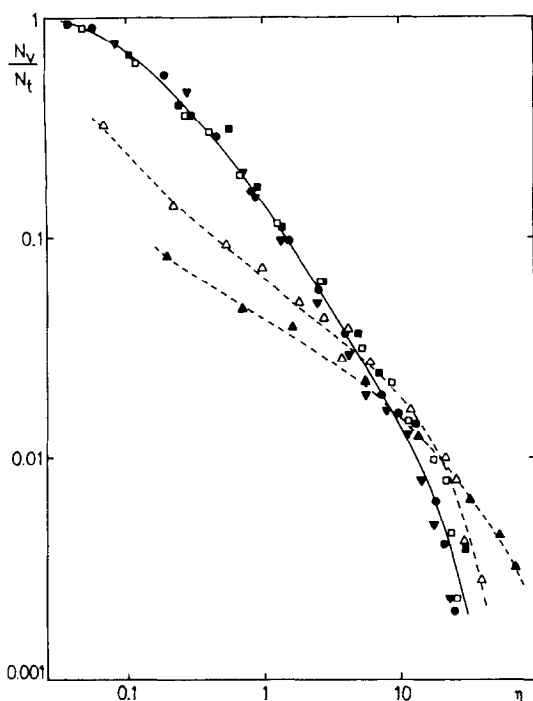


FIG. 6. Tests of self-preservation of platinum particles on unactivated and activated carbon supports following heat treatment of samples prepared at 773 K to higher temperatures. Unactivated support: ●, as prepared; □, 48 hr at 920 K; ■, 48 hr at 1020 K. Activated support: ▲, as prepared; △, 24 hr at 920 K; ▼, 48 hr at 1020 K.

Figure 6 represents such diagrams for both the activated and unactivated carbon substrates. As expected from the size distribution of the particles given in Fig. 4, the unique spectrum is already obtained at the preparation temperature (773 K) when the homogeneous carbon support is used. For the heterogeneous support, however, the equilibrium spectrum is reached only at higher temperatures. Thus, the size distribution on the heterogeneous substrate is not self-preservative in the early stages of sintering but tends toward the same equilibrium spectrum as that for platinum particles on the homogeneous support. From a physical point of view, this means that above a given thermal energy threshold, which depends on the properties of the

substrate, interaction between the particles and the surface is no longer the determining factor. Rather, the dispersed phase arranges itself in an equilibrium state, regardless of the condition of the substrate.

## CONCLUSIONS

The size distribution of platinum particles supported on carbon exhibits considerable differences depending on the extent of heterogeneity of the substrate. On an unactivated, graphitized (that is, homogeneous) carbon surface, particle size follows a log-normal distribution even at preparative temperatures as low as 773 K. In contrast, on an activated (that is, heterogeneous) carbon surface, very small particles are observed following preparation at 773 K which do not follow a log-normal distribution. Results suggest that at higher temperatures sintering tends to produce an equilibrium size distribution of platinum particles, regardless of the extent of heterogeneity of the carbon support.

## ACKNOWLEDGMENT

Discussions on electron microscopy techniques with Dr. A. Eckardt are appreciated.

## REFERENCES

1. Ehrburger, P., Mahajan, O. P., and Walker, P. L., Jr., *J. Catal.* **43**, 61 (1976).
2. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).
3. Anderson, J. R., "Structure of Metallic Catalysts," p. 358. Academic Press, New York and London, 1975.
4. Sprys, J. W., Bartosiewicz, L., McCune, R., and Plummer, H. K., *J. Catal.* **39**, 91 (1975).
5. Fukami, A., and Adachi, K., *J. Electron Microsc.* **14**, 112 (1965).
6. Flynn, P. C., Wanke, S. E., and Turner, P. S., *J. Catal.* **33**, 233 (1974).
7. Granqvist, C. G., and Buhrman, R. A., *J. Catal.* **42**, 477 (1976).
8. Flynn, P. C., and Wanke, S. E., *J. Catal.* **37**, 432 (1975).

9. Wynblatt, P., and Tae-Moon, A., in "Sintering and Catalysis, Materials Science Research" (G. C. Kuczynski, Ed.), Vol. 10, p. 83. Plenum Press, New York, 1975.
10. Prado, G., and Lahaye, J., *J. Phys. Chem.* **4**, 483 (1975).
11. Wong, S., Flytzani-Stephanopoulos, M., Chen, M., Hutchinson, T. E., and Schmidt, L. D., *J. Vacuum Sci. Technol.* **14**, 452 (1977).
12. Thomas, J. M., and Walker, P. L., Jr., *J. Chem. Phys.* **41**, 587 (1964).
13. Ruckenstein, E., and Pulvermacher, B., *J. Catal.* **29**, 224 (1973).
14. Swift, D. L., and Friedlander, S. K., *J. Colloid Sci.* **19**, 621 (1964).