Crystallite Growth of Platinum Dispersed on Graphitized Carbon Black

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The growth of platinum crystallites supported on graphitized carbon during heat treatment was considered in terms of models assuming surface diffusion of the crystallites (Smoluchowski model) and migration of platinum atoms (Ostwald ripening model) for the rate determining steps. Analyses of the mechanisms suggested that for the Ostwald ripening model, the rate constant, k, for the decrease in Pt surface area during sintering was independent of ϕ, the total Pt crystallite volume per unit area of support, whereas in the Smoluchowski model k was proportional to ϕ. By investigating the gas-phase sintering of supported catalysts with different Pt surface concentrations, it was possible to study the dependence of k on ϕ and, hence, to distinguish the sintering mechanism. It was concluded that the sintering of Pt on graphitized carbon can be rationalized in terms of a Smoluchowski mechanism in which Pt crystallites migrate from trap sites on the support and coalesce on the carbon surface.

Crystallite growth of metal catalysts on supports at high temperatures has been reported frequently (*1–5*), but the equations which have been used to describe the concomitant metal surface area decrease with time have only recently been given detailed physical interpretations. Two basically different mechanisms can be proposed for metal transport on the surface of the support to produce crystallite growth. Firstly, it has been suggested that discrete metal crystallites (clusters) migrate on the support in a process analogous to two-dimensional Brownian motion (*6, 7*). On collision, the crystallites coalesce. Depending on the sintering conditions, either surface diffusion or coalescence of crystallites may be rate limiting. Ruckenstein and Pulvermacher (*8, 9*) have derived the relationship between the crystallite size distribution (or exposed metal surface area) and heat treatment time based on this model and have applied their equations to several experimental studies for platinum on alumina catalysts. The same mechanism has also been invoked by Phillips *et al.* (*7*) to describe the crystallite growth observed upon annealing thin evaporated discontinuous gold films.

The second mechanism used to describe metal crystallite growth involves evaporation of atoms from small crystallites and condensation on larger ones in a process akin to the Ostwald ripening of dispersed precipitates in solution. The atoms may diffuse either on the surface of the support as adatoms or in the gas phase. Somorjai (*10*) developed equations from the Ostwald ripening mechanism to correlate low-angle X-ray diffraction observations of the growth of well-dispersed platinum particles on alumina at 600 and 700°C, while recently Huang and Li (*11*) have used the same model in reporting electron-micrographic observations of sintering for large (1500–3000 Å) particles of platinum on alumina at 900°C.

In considering the possible contribution

of each mechanism to the transport of metal during sintering, supportive evidence for the occurrence of both crystallite migration and adatom diffusion can be cited. For example, the mobility of metal crystallites on support surfaces has been frequently demonstrated in electron microscopic studies of discontinuous metal films. Bassett (*12*) has observed translation of copper and silver islands on amorphous carbon and graphite at 252°C while Phillips *et al.* (*7*) inferred motion and coalescence of gold islands (up to 100 Å in diam) on supports of silicon monoxide and amorphous carbon in the temperature range 227–427°C. More recently, Masson *et al.* (*6*) have shown that islands of gold or aluminum (20–50 Å in diam) can execute random walks on potassium chloride substrates at 70°C. Thomas and Walker (*13*) also reported evidence for metal crystallite motion on carbon substrates.

It may be argued that at temperatures where sintering of supported platinum catalysts is commonly reported, coalescence of contiguous platinum particles can be rapid since both McKee (*14*) and Khassan *et al.* (*15*) have shown that platinum blacks in a hydrogen atmosphere rapidly lose a large fraction of their surface area at temperatures as low as 200°C. This would imply that, for the sintering of supported platinum catalysts between 500 and 600°C, crystallite migration rather than coalescence should be the rate limiting process.

Direct experimental evidence for the occurrence of atomic evaporation and condensation processes is less abundant. This mechanism has been dismissed in some previous discussions (*7–9*) on the basis of the relatively high energetic requirements. Certainly, the gas-phase path can be readily eliminated as a possibility for platinum crystallite growth at temperatures in the vicinity of 700°C, since the rates of evaporation for bulk platinum are too low (*16*). Emelianova and Hassan (*17*) found, however, that with rapid quenching of Pt supported on Al_2O_3 following a heat treatment *in vacuum* at high temperatures (400–800°C) the platinum surface areas showed

large increases. This was interpreted as due to quenching of an atomic phase produced by dissociation of microcrystals at these temperatures. Stabilization of adatoms on the support surface may render surface diffusion considerably less demanding energetically so that, without detailed knowledge of the surface flux of atoms under experimental conditions, this mechanism cannot be conclusively eliminated.

Since both crystallite migration and Ostwald ripening are possible, a close examination of the relationship between crystallite size distribution or surface area and heat treatment time may be necessary in order to establish the sintering mechanism. Rate expressions for the surface migration mechanisms have been derived as extensions of the Smoluchowski (*18*) coagulation theory. Using a treatment analogous to that applied by Swift and Friedlander (*19*) for the coagulation of hydrosols, Ruckenstein and Pulvermacher (*8, 9*) described the rate of sintering as a decrease in the surface concentration of crystallites due to a series of two body collisions, which were summed over all collisions occurring for a heterogeneous particle size distribution. Converting from crystallite size to surface area, they obtained a rate law for the decrease in exposed metal surface area of the dispersion as a function of time, where the order with respect to surface area varied between 2 and 6, depending on whether crystallite coalescence or surface diffusion on the substrate was rate limiting. The general form of the integrated rate expression is given as

$$\frac{1}{S^n} = \frac{1}{S_0^n} + kt, \tag{1}$$

where S_0 and S represent the metal surface areas per unit volume, before sintering and at time t, respectively. The constant, k, is directly proportional to ϕ, defined as the total volume of metal per unit area of support. Variation in the order, n, with respect to the surface area resulted from the introduction of a rate constant having a variable dependence on crystallite size. This variation in order was used to categorize a number of experimentally observed

rate laws. It was argued that the rates of surface diffusion for crystallites on a substrate would be inverse functions of the crystallite radii. Resultant solutions of the rate law produced n values between 3 and 5 for surface migration of crystallites (8, 9). Values of n between 1 and 2 were taken to indicate that crystallite coalescence was rate limiting, since these values are deduced from previously reported data for sintering of unsupported metals. Platinum crystallites on alumina heated in a hydrogen atmosphere give derived values for n of 5 (3) and 7 (4) at 500 and 482°C, respectively, inferring crystallite surface diffusion controlled sintering. At higher temperatures (1, 20) in air, an n value of 2 was calculated, indicating that intercrystallite coalescence for the supported metal was rate limiting.

Phillips, Desloge, and Skofronick (7) have also assumed crystallite surface diffusion occurred during the sintering of gold on carbon and on silicon monoxide. Their kinetic equations were derived from a model in which gold islands with thermal energy $E > E_0$ could escape from trap sites and were therefore free to move on the surface. Crystal growth resulted from collisions between mobile and stationary gold islands. A rate law for the decrease in the number of crystallites with time was obtained which was second order in the crystallite concentration. The rate constant was a function of the crystallite radius, analogous to the treatment of Ruckenstein and Pulvermacher (8, 9). Hence the integrated rate law from their treatment had the same form as Eq. (1), where n had a value of $\frac{7}{2}$ and k was directly proportional to the metal catalyst content.

The Ostwald ripening mechanism supposes that evaporation of atomic species from small crystals and condensation on larger ones occurs by virtue of the difference in solubilities as predicted by the Gibbs-Thomson equation. Chakraverty (21) has treated this case for annealing of metal films, where surface diffusion of adatoms is rate limiting and has obtained an expression which is related in form to (1), i.e.,

$$r_k = r_{k_0}\left[1 + \frac{t}{t_s}\right]^{1/4}, \qquad (2)$$

where r_{k_0} and r_k are the critical radii of the particle (radius at which the particle neither dissolves nor grows) at time zero and at time t, and t_s is a constant which is independent of ϕ and inversely proportional to $r_{k_0}^4$. If one substitutes, as do Huang and Li (11), the mean particle radius for the critical radius and converts to surface area (assuming spherical particles), an equation similar to (1) is obtained where $n = 4$. This equation, however, differs from (1) in an important respect, since the constant k in this case is independent of the total volume of metal per unit area of support (ϕ). Huang and Li (11) obtained a fit of data for the annealing of platinum on alumina to Eq. (2) but were unable to reconcile their observed particle size distributions with those predicted by the treatment of Chakraverty.

Dunning (22) has solved the simpler case for Ostwald ripening of dilute dispersed precipitates in solution. The rate expression resulting from this treatment again is related to (1), i.e.,

$$N = N_0\left[1 + \frac{t}{\tau}\right]^{-1}, \qquad (3)$$

where N_0 and N represent the total number of particles initially and at time t, respectively; τ is a constant which is also independent of ϕ and directly proportional to r_k^3. If it can be assumed that the solution for the three-dimensional problem is similar to the two-dimensional problem of catalyst sintering, it may readily be shown that Dunning's equation can also be expressed in the form of Eq. (1), where $n = 3$ and k is independent of ϕ. The case of the dilute dispersion had previously been solved by Greenwood (23) using an approximation, and Somorjai (10) applied an extension of this treatment to observations for platinum crystallite growth on an alumina support. More recently, Wynblatt and Gjostein (24) used a treatment similar to Somorjai's to explain values of $n = 12$ which were obtained when applying an equation of the form of (1) to their data

for the sintering of sputtered platinum films on alumina.

Finally, we should note the sintering model developed by Flynn and Wanke (25), also based on an Ostwald ripening mechanism, predicts considerable variation in the n value for a power law fit of sintering and stresses the effect of crystallite size distribution on the sintering rate.

It is concluded that both the Smoluchowski collision model and the Ostwald ripening mechanism for sintering of supported metal catalysts result in rate laws which have the same form. Since the accuracy with which the exposed metal area can be determined is not great, it is consequently difficult to identify the sintering mechanism from a determination of reaction order. On the other hand, as pointed out by Dunning (22), a significant difference exists between the two mechanisms in the dependence of the rate constant, k, on ϕ (the metal concentration on the catalyst). Various forms of Eq. (1) for the different mechanisms have been collated in Table 1.

In the present paper, measurements are reported for the decrease in surface area upon sintering of platinum crystallites dispersed on graphitized carbon blacks. Supported catalysts with widely different surface concentrations of platinum were studied in an attempt to use this variable

to distinguish between the Ostwald ripening and Smoluchowski collision models for sintering. Electrochemical techniques allowed rapid determinations for the platinum surface areas on carbon (26). Furthermore, it was felt that an understanding of the interactions between the metal particles and the support might be aided by the extensive previous characterizations of the surfaces of graphitized carbon blacks (27, 28). The present work also represents an extension of our previous interest in sintering of unsupported platinum blacks (29, 30).

EXPERIMENTAL DETAILS

Catalyst Preparation

Three samples of platinum supported on graphitized Vulcan XC-72 carbon black (Cabot Corp.) were examined. Samples with 5.0 and 20 wt% platinum were prepared by an impregnation technique, in which solutions of $Pt(NH_3)_2(NO_3)_2$ were evaporated to dryness and subsequently decomposed in air at 260°C for 3 hr. Another sample with 12 wt% platinum was prepared by adsorption of a colloidal suspension of platinum on the carbon. After catalyst preparation, the graphitized carbon black surface contains small concentrations of surface oxide < 0.5% which

TABLE 1
EQUATIONS FOR SINTERING RATES OF SUPPORTED METAL CATALYSTS

$$\frac{1}{S^n} = \frac{1}{S_0^n} + kt$$

Reference	Mechanism	Rate determining process	n	k Constant
Ruckenstein and Pulvermacher (8, 9)	Crystallite Migration	Coalescence Surface diffusion	2–3 3–5	$\alpha\phi$ $\alpha\phi$
Phillips, Desloge, and Skofronick (7)	Crystallite Migration	Surface diffusion	½	$\alpha\phi$
Chakraverty (21)	Ostwald ripening Ostwald ripening	Surface diffusion Interface transfer	4 2	Independent of ϕ Independent of ϕ
Dunning (22)[a]	Ostwald ripening	Surface diffusion	3	Independent of ϕ

[a] Solution for three-dimensional process.

ϕ = Total volume of metal per unit area of support.

have been extensively discussed elsewhere (27).

Heat Treatment

The prepared catalyst sample ($\sim$100 mg) was placed in a quartz tube muffle furnace and purged initially with nitrogen at room temperature; then hydrogen was passed over the catalyst at 350°C for 30 min, after which the temperature was raised to 500°C. This ensured that the platinum and carbon surfaces were well reduced prior to the sintering experiments. Analysis showed that neither surface area loss nor methanation of the carbon surface occurred at this temperature. The tube was removed from the furnace, flushed with nitrogen, and catalyst samples replaced in the furnace at the sintering temperatures. After heat treatment for various lengths of time, the samples were removed from the furnace and cooled to room temperature in a nitrogen atmosphere. A different catalyst sample was heat treated for each of the various times investigated, so every sample was subjected to only one heating and cooling cycle.

Some sintering experiments were conducted in a hydrogen rather than a nitrogen atmosphere, and at high temperatures (>600°C) some methanation of the carbon surface could be detected.

Surface Area Measurements

In order to measure the platinum crystallite surface area, the catalyst samples were fabricated into PTFE-bonded porous electrodes and subjected to linear potentiodynamic sweeps (26) in $1\,M$ H_2SO_4 at room temperature. This electrochemical technique yields a measurement for the surface charge associated with chemisorbed hydrogen on the platinum and hence of platinum crystallite size (26).

The platinum crystallite size distributions for selected samples before and after sintering were determined from electron micrographs obtained on a Phillips 200 electron microscope. Specimen preparation and measurements of the platinum particle sizes were the same as reported by Fornwalt and Kinoshita (31).

The surface area of the graphitized carbon black support measured by BET nitrogen adsorption was 80 m^2/g and was shown not to vary significantly during heat treatment.

RESULTS AND DISCUSSION

Figure 1 shows the decrease in exposed metal surface area with time for three different concentrations of platinum supported on carbon. At 600°C, sintering in both H_2 and N_2 atmospheres gave similar curves for platinum crystallite surface area changes with time. Samples with 5 and 12 wt% platinum suffered a gradual decrease in area with time in contrast to the very rapid decrease evident for the sample with 20 wt% platinum. (At 500°C in hydrogen and in vacuum, there were no appreciable surface area decreases for the platinum crystallites.) Confirmation that the decrease in platinum crystallite surface area resulted from crystallite growth was obtained from a sequence of electron micrographic observations, typically shown in Fig. 2. Surface areas calculated from crystallite size distributions were in reasonable agreement with those measured electrochemically (26).

On the basis of the previous discussion, both processes for material transport, Ostwald ripening, and Smoluchowski collision appear to be possible for platinum sintering under the conditions of the pres-
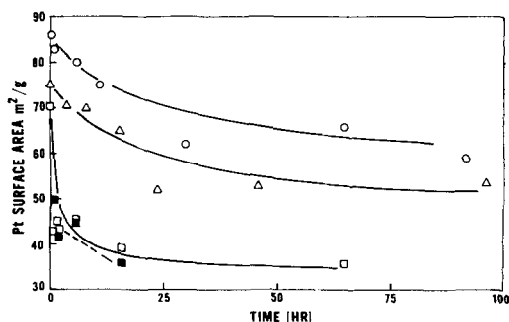

FIG. 1. Decrease in platinum crystallite surface area for platinum crystallites supported on graphitized carbon black. 600°C. ($\bigcirc$) 5; ($\triangle$) 12; ($\square$) 20 wt% Pt in N$_2$. ($\blacksquare$) 20 wt% Pt in H$_2$. Dashed line corresponds to decay from an initial 45-m^2/g Pt datum after trap site saturation.
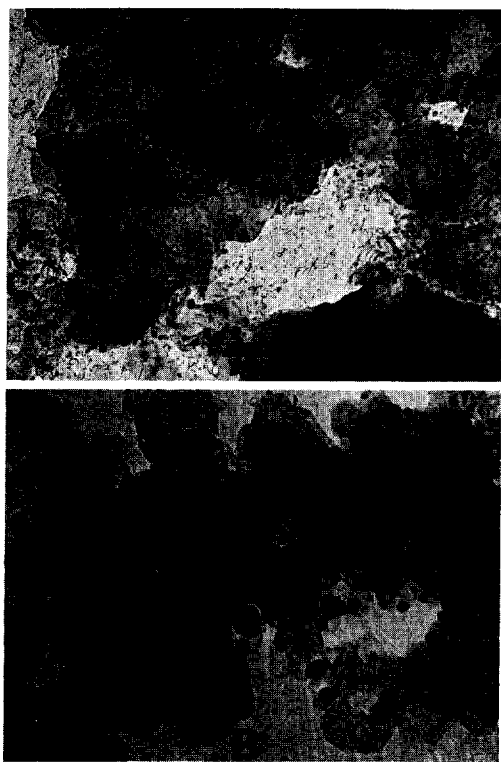
FIG. 2. Electron micrographs of 20 wt% Pt on graphitized carbon. Magnification 220,350×. Plate A: Initial. Plate B: After 16 hr at 600°C in N_2.
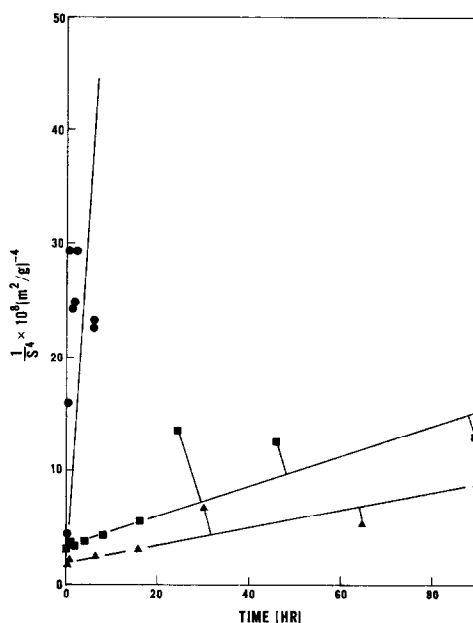

FIG. 3. Sintering of platinum crystallites on graphitized carbon plotted according to Eq. (1) with $n = 4$ for surface diffusion of the crystallites. (▲) 5; (■) 12; (●) 20 wt% Pt.

ent experiments. Therefore, rate laws of the form of Eq. (1) should apply to the data, with the dependence of the rate constant on the platinum concentration or initial surface area being a test for the relative contributions of either processes to sintering.

It was evident from attempts to fit the data of Fig. 1 to equations of the general form of (1) that the value of n required to fit the curves was high, due particularly to the very marked curvature for the experiment with 20 wt% Pt. The confidence value with which the fit could be established was not great, due to the high value of n, coupled with the generally low accuracy of surface area measurements. Moreover, when the n values were varied between 2 and 8 to fit the data according to Eq. (1), the rate constants derived from the experimental slopes of the functions showed a greater dependence on ϕ than could be pre-

dicted by either sintering mechanism. The problem is illustrated in Fig. 3 where plots of Eq. (1) for $n = 4$ are shown and in Table 2 where the calculated rate constants are listed. Obviously, k was not constant and therefore was inconsistent with the Ostwald ripening mechanism, nor was the fit improved when n had values up to 8. Likewise, a constant value was not obtained when k was normalized for ϕ, the total volume of platinum per unit area of support, as is required by the Smoluchowski collision mechanism.

An explanation for this anomaly may lie in the character of the particle size distribution assumed by the supported platinum and in the platinum crystallite interaction with the carbon surface. Swift and Friedlander [19] have stressed that the kinetics for coagulation of polydisperse hydrosols are second order with respect to the particle concentration only if the particle size distribution functions conforms to a unique, dimensionless cumulative distribution function at all times. The test for this "self-

TABLE 2

RATE CONSTANTS FOR SINTERING OF PLATINUM CRYSTALLITES ON
CARBON AT 600°C USING EQ. (1), $n = 4$

Wt% Pt	$\phi \left(\dfrac{cm^3\ Pt}{cm^2\ surface} \right) \times 10^8$	S_0 (m^2/g Pt)	k(m^2/g)$^{-4}$ hr^{-1} $\times 10^9$	$\dfrac{k}{\phi}$
5	0.3	85	0.72	0.23
12	0.8	76	1.45	0.18
20	1.4	70	72	5.1
20[a]	1.4	45	3.1[a]	0.21

[a] Based on an initial rate, assuming $S_0 = 45$ m^2/g (see text).

preservation" of the function requires that plots of

$$\sum_i^\infty N_{vk}/N_\infty \text{ vs } \frac{V_k N_\infty}{\phi}$$

should be coincident. N_∞ is the total number of particles; N_{vk}, the number of particles of volume greater than V_k. Applying a related treatment to sintering of catalysts by the Smoluchowski mechanism, Ruckenstein and Pulvermacher (8, 9) showed that, regardless of the initial crystallite size distribution, the crystallite size distributions calculated from their equations for surface diffusion controlled sintering could be represented by a similar unique spectrum after short sintering times. They demonstrated that platinum on silica and platinum on alumina catalysts prepared by Wilson and Hall (32) had distributions coincident with the unique spectrum calculated from the collision equation and pointed out that this was to be expected, since sintering would occur during the high-temperature reduction employed in the catalyst preparation. When the "self-preservation" test was applied to the particle size distribution for the 20 wt% Pt on carbon catalyst, it was apparent (Fig. 4) that the dimensionless cumulative distribution function for the fresh sample was *not* coincident with that of the sintered sample.

The sintering equations should rightly be applied only after some short time when the unique spectrum had been achieved. The data in Fig. 1 suggest strongly that

this time was of the order of 1–2 hr, during which the sharp drop in surface area for the 20 wt% Pt on carbon sample had been completed. With this in mind, an initial slope was constructed for the 20 wt% Pt data assuming a value for S_0 of 45 m^2/g and using the differential form of Eq. (1):

$$-\frac{dS_0}{dt} = kS_0^5.$$

The value of k/ϕ so derived was in agreement with the corresponding values at lower platinum loadings (Table 2) indicating that surface diffusion of the platinum crystallites on the carbon surface was rate controlling. The constructed line in Fig. 1 appeared to conform to the experimental curve if it was assumed that the rate equation was obeyed only after an initial rapid decrease in area.

This interpretation for the sequence of curves in Fig. 1 implies that, as the concentration of metal crystallites on the carbon surface increased, the initial distribution of crystallite sizes departed abruptly from the unique spectrum assumed at lower concentrations and also after high-temperature sintering. The inhomogeneity of the carbon surface might be the origin of this behavior. Phillips, Desloge, and Skofronick (7) developed the kinetics for gold particle growth on carbon in terms of a surface populated largely by immobile particles trapped in potential wells requiring an activation energy to escape. Only the small number of particles with energy in excess of this value are mobile and active in promoting collision. At 300°C the
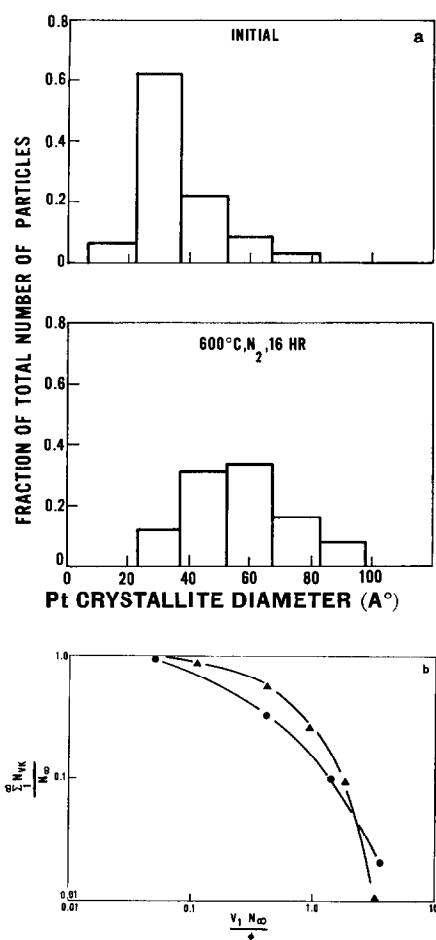
FIG. 4. Test for "self-preservation" of the platinum crystallite distribution. 20 wt% Pt on graphitized carbon. 600°C. (a) Histograms of initial and final (16 hr) distributions. (b) (●) Initial; (▲) final.

surface particle concentration was approximately $1 \times 10^{12}/cm^2$. This was close to the value for the density of trapping sites. In the present experiments, at 600°C, the initial metal crystallite concentrations were $1.5 \times 10^{11}/cm^2$ for 5 wt% Pt on carbon and $4.5 \times 10^{11}/cm^2$ for 20 wt% Pt on carbon. One might expect that, at the higher temperatures and on a graphitized carbon surface, the number of trapping sites would be less than on the amorphous carbon supports prepared by Phillips et al. (7). Thus on heat treatment at 2700°C the surface planar domain size for carbon

black can increase from about 20 to 80 Å (28), which is indicative of the average length for graphitic basal plane order on the carbon surface as determined by X-ray diffraction.

The boundaries of basal planes are the sites for carbon oxide species and may be the trapping sites required for platinum crystallite immobilization. Studies of nucleation and growth of vapor deposited metal films have revealed that stabilization of metal nuclei can occur at point defects on the surfaces of inorganic salts in addition to the commonly observed decoration effects at major step locations (33). Very little evidence for decoration could be seen in electron micrographs of the present platinum on carbon catalysts so that dislocations occurring at the edges of planar domains might act as trapping sites.

One may therefore conjecture that, with the 20 wt% Pt on carbon catalyst containing 4.5×10^{11} crystallites/cm^2 carbon surface, the trap site density was exceeded. If this is so, then an initial population of unstable particles is produced which would sinter rapidly at higher temperatures until the crystallite concentration matched the trap site density. At this point, the regular surface diffusion controlled sintering process of the type described by Phillips, Desloge, and Skofronick (7) could ensue with a higher activation energy required to move crystallites out of the trap sites. This point would appear to be reached after 2 hr of sintering for the 20 wt% Pt on carbon catalyst shown in Fig. 1. While speculative, these conjectures serve to emphasize that a full understanding of the sintering mechanism must recognize the relationship between crystallite concentration and support surface structure.

The curves relating surface area decrease with time, as a function of temperature, also exhibited abrupt changes in form which would originate from the effect of temperature on the trapping site density. Thus, Fig. 5 shows a 5 wt% Pt catalyst where the surface area loss at 600°C was smoothly monotonic, whereas at 700°C a rapid initial loss was seen, similar to that observed for 20 wt% Pt at 600°C. No at-
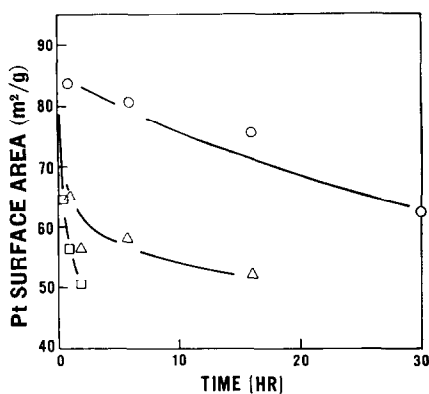
FIG. 5. Decrease in platinum crystallite surface area as functions of time and temperature. 5 wt% Pt on graphitized carbon black. (○) 600; (△) 700; (□) 800°C.

tempt was made to derive an activation energy using the data at higher temperature, but the equation of Phillips, Desloge, and Skofronick (7) (for sintering by the Smoluchowski mechanism) enabled an activation energy to be calculated from data at a single temperature. Applying this treatment to the results at 600°C for 5 wt% Pt on carbon, an activation energy of 1.8 eV was obtained. This was close to values obtained for gold on carbon (1.34 cV at 300°C) and gold on silicon (1.86 eV at 447°C) by Phillips *et al.* (7). The activation energy obtained from the data of Hermann *et al.* (1) was 1.7 eV at 564°C for platinum on alumina.

It appears, therefore, that the data for the sintering of platinum on carbon can be rationalized in terms of a Smoluchowski mechanism in which platinum crystallites migrate from trap sites and coalesce on the surface of the carbon.

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