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Crystallite Growth of Platinum Dispersed on Graphitized Carbon Black

II. Effect of Liquid Environment

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The effect of various liquids on the growth of platinum crystallites dispersed on graphitized carbon has been determined from electrochemical surface area measurements. Although significant crystallite growth was not observed on exposure to hydrogen gas at temperatures less than 600°C, rapid growth occurred below 200°C in the presence of a liquid environment. Crystallite growth rates were independent of the platinum content on the catalyst and of the electrode potential. Furthermore, the nature of the liquid environment did not appear to have an influence on the rate of Pt crystallite surface area loss. When fitted to a simple power law, the order of the rate process lay between 11 and 13, and the activation energy was 21 kcal/mole. The implications of these experimental results are discussed with reference to recent theoretical models for the mechanism of crystallite growth. It is concluded that the evidence strongly suggests that two-dimensional Ostwald ripening (the migration of platinum atoms on the carbon surface) is the process whereby platinum is transferred from one crystallite to another, producing a decrease in the Pt crystallite density and surface area.

INTRODUCTION

The thermal sintering of supported metal catalysts was discussed in a number of recent publications (*1–4*). These papers have been concerned primarily with the derivation of the relationships between particle size or particle size distribution and sintering time, based upon a proposed model for the sintering process. Two basically different mechanisms were considered; the Smoluchowski collision model in which crystallites migrate, collide and coalesce on the support surface and the Ostwald ripening model in which metal crystallites dissociate to metal atoms which then diffuse to and associate with larger particles.

Earlier treatments of the collision model by Ruckenstein and Pulvermacher (*1, 2*) and the ripening model by Chakraverty (*4*) have resulted in simple power law rate equations for the sintering process which are similar in form, i.e.,

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

where S_0 and S are the metal surface areas initially and at time t, and k is a constant. The exponent, n, varies for each model and may be as large as 8. It was, therefore, difficult to distinguish the sintering mechanism by means of Eq. (1). Furthermore, the value of the exponent, n, required to fit the experimental data was found to be as high as 15 (*3*), which could not be explained by the earlier derivations of the rate law, Eq. (1).

By invoking a requirement for nucleation of steps on crystal facets, for crystal growth either by particle migration or by atom diffusion, Wynblatt and Gjostein (*2*) have introduced an exponential dependence of the rate constant for sintering on r, the crystallite diameter. In this case the observed value of n in Eq. (1) will vary with time and reach high values for large values of r. Flynn and Wanke (*3*) also predicted large values of n as a result of the application of the Ostwald ripening model to sintering of catalysts with a wide particle size distribution.

The manner in which the particle size distribution changes with time was predicted for the various sintering models and was used to differentiate the sintering mechanisms (*1*, *3*). Unfortunately, experimental difficulties in accurately defining the particle sizes may render this method a somewhat inaccurate indicator (*5*, *6*). One case in which the Ostwald ripening mechanism can clearly be identified arises when the metal dispersion *increases* in the early stages of sintering. Emel'yanova and Hassan (*7*) have reported this observation for the sintering of Pt on Al_2O_3 catalysts.

Another major difference between the two sintering models is in the rate constant, k, of Eq. (1), where Ostwald ripening is independent of metal loading, whereas the Smoluchowski model is directly proportional to catalyst metal loading (*8*). This feature was used by Bett *et al.* (*9*) to identify Pt crystallite migration as the mechanism for surface area loss in the thermal gas-phase sintering of platinum supported on carbon catalysts. It should be noted that the recent treatment by Flynn and Wanke (*3*) of the Ostwald ripening model for sintering, departs from prior treatments based directly on the three-dimensional analogue, crystallite growth in solution, and obtains, under certain conditions, a dependence of the rate of crystallite growth on metal loading.

The present paper compares the sintering of platinum on carbon in liquid- and gas-phase environments. The dependence of the sintering rate on Pt loading was examined and in addition, the differences between gas- and liquid-phase sintering of supported Pt electrocatalysts yielded a valuable insight into the rate limiting process in both cases. Platinum supported on carbon is of interest as an electrocatalyst which, because of its high electrical conductivity, allows control of potential as an added variable in sintering studies in the liquid phase.

Connolly *et al.* (*10*) previously had reported large decreases in the surface area of platinum crystallites dispersed on carbon in various electrolytes at 100–200°C—temperatures far below those where significant loss of surface area could be induced in the gas-phase. The surface area loss was not caused by dissolution of platinum since no platinum was found in solution and no loss of platinum from the catalyst was measured. A detailed discussion of the mechanism to explain the Pt surface area loss was not presented. Extensive surface area losses occurred under similar conditions when unsupported platinum black was sintered electrochemically (*11*, *12*). In this case it was concluded that particle growth occurred by surface diffusion of platinum atoms on the individual crystallites, from sites of higher to lower surface energy. Supported platinum on carbon shows large differences in the rates of crystallite growth for gas and liquid-phase sintering. Unsupported platinum blacks have been shown by McKee (*13*) and Kassan *et al.* (*14*) to undergo significant surface area losses, when heated in a reducing atmosphere at 100–200°C. The latter sintering rates are of a comparable magnitude to sintering rates for platinum black in the liquid-phase over the same temperature range (*11*, *12*).

EXPERIMENTAL DETAILS

Catalyst Preparation

Samples of 5 and 20 wt% Pt on graphitized Vulcan XC-72 carbon black (Cabot

Corp.) were prepared by an impregnation technique. Solutions of $Pt(NH_3)_2(NO_2)_2$ in dilute nitric acid, of suitable concentration to give the desired metal content, were evaporated to dryness on the carbon and subsequently decomposed in air at 260°C for 3 hr. After catalyst preparation, the graphitized carbon surface contains small concentrations of carbon surface oxide, $<0.5\%$, which has been discussed extensively elsewhere (*15*).

Surface Area Measurements and Sintering Experiments

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 (*16*) in 1 *M* H_2SO_4 at room temperature. This electrochemical technique yields a measurement of the coulombic charge associated with chemisorbed hydrogen on the platinum and, assuming 210 $\mu C/\text{real cm}^2$ Pt, the Pt surface area and hence the crystallite size can be determined.

Care was taken to terminate the potentiodynamic sweep at a low potential (0.05 V *vs* n.h.e.) so that the platinum surface was oxide free. The electrode was then washed in distilled water and placed in a three electrode cell containing 96% phosphoric acid at controlled temperature. The platinum-on-carbon electrodes were held at any desired potential with respect to a hydrogen reference electrode in the same electrolyte by means of a potentiostat. After a given period of time, the electrodes were removed from the high temperature cell, washed with distilled water and then the surface area of the platinum was measured at room temperature in dilute acid.

The surface area of the supporting graphitized carbon, determined from the double layer capacitance (*15*), did not differ from the initial value of 70 m^2/g during the sintering experiments.

RESULTS

The decrease in surface area of platinum dispersed on carbon was measured after the electrodes were immersed in hot, concentrated phosphoric acid for various time periods at controlled potential. Typical results shown in Fig. 1 indicate a rapid initial decrease of the platinum crystallite surface area for catalysts containing 5 and 20% metal at 100 and 160°C. After a short time, the rate of surface area loss decreased to a relatively constant value which appeared to be dependent on temperature but not on platinum concentration of the catalyst. Measurements taken up to 25,000 min confirmed that the platinum surface areas were not constant but continued to decrease with time.

Due to the very sharp discontinuity in slope, a high value of n was evidently required for the data in Fig. 1 to be fitted by the simple power law [Eq. (1)]. Fitting to the function was accomplished by the method of Hoogschagen and Zweitering (*17*) in which Eq. (1) was rearranged to give

$$\frac{1}{kS^n} = \tau_0 + t. \qquad (2)$$

The logarithm of the surface area was plotted against the logarithm of the sintering time, $t + \tau_0$. Values of $\tau_0 = 1/kS_0^n$ were found by trial and error to give a best set of parallel lines for each temperature. The best fit lines plotted in Fig. 2 showed small deviations for the initial data points at 160°C. The slopes corresponded to a value of n from 11 to 13 for the 5 and 20% catalysts and the activation energy, E_a, calculated from values for τ_0 was 21 kcal/mole for each catalyst. Although these values were not well defined by plots such as shown in Fig. 2, the validity of the calculation was supported, in an alternate treatment of the data, by plotting values of $\log S/S_0$ vs $1/T$, at a constant and large value of t, i.e., the quasi-limiting values for surface area. The slope of the plot gave a

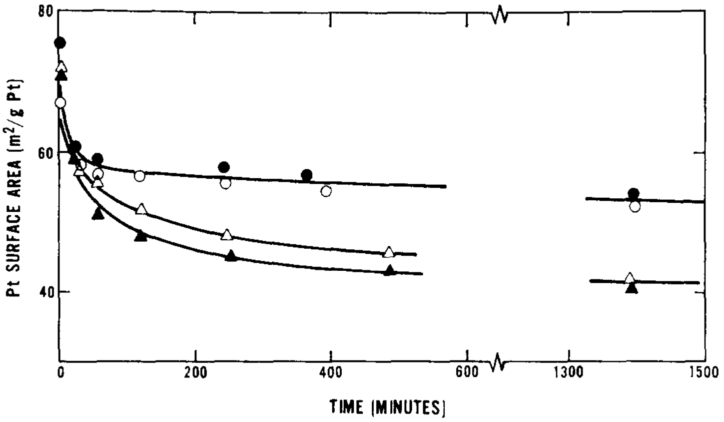

FIG. 1. Effect of temperature and platinum metal content on crystallite growth of platinum on carbon in 96% H_3PO_4 at 0.8 V. (●) 5 wt% Pt, 100°C; (○) 20 wt% Pt, 100°C; (△) 5 wt% Pt, 160°C; (▲) 20 wt% Pt, 160°C.

value for E_a/n of 1.7 kcal/mole, consistent with the previous treatment. Figure 1 also indicates no significant effect of a fourfold change in supported metal concentration of the catalyst on the rate of sintering. Due to the large value of n and the form of Eq. (1), little change in the plateau value of S/S_0 would be expected even if k were proportional to metal loading, since

$$S/S_0 = \frac{k^{1/n}t^{1/n}}{S_0} \quad \text{for} \quad S_0{}^n kt \gg 1.$$

It was difficult to determine k from the surface area vs time curves since the initial slopes were so steep, but careful inspection of the data did not suggest any dependence of k on loading. This observation is in contrast with the gas-phase sintering data (*9*) where, in a hydrogen atmosphere at 600°C, large changes in the rates of sintering of these catalysts were observed as the metal loading was varied between 5 and 20%, consistent with a direct proportionality of the rate constant, k, on loading. The present

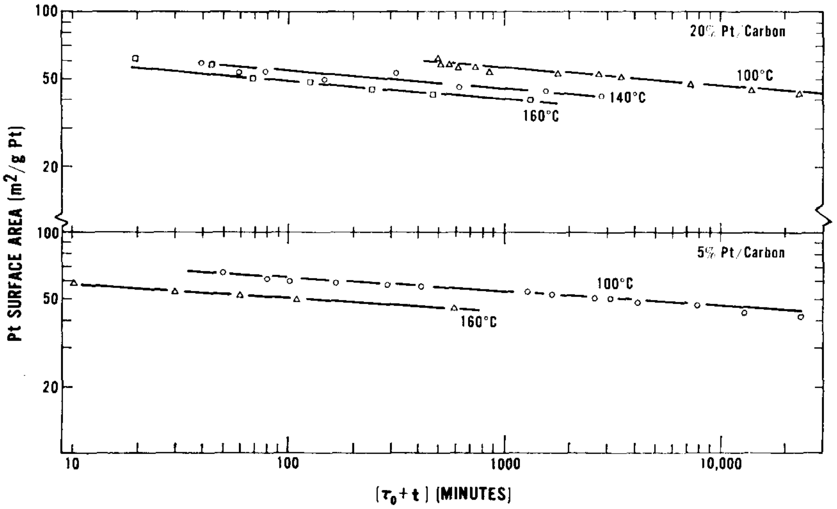

FIG. 2. Plot of eq. (2); $1/kS^n = \tau_0 + t$, for sintering of platinum on graphitized carbon black in 96% H_3PO_4, 0.8 V. 20% Pt: (△) 100°C, τ_0 = 500; (○) 140°C, τ_0 = 30; (□) 160°C, τ_0 = 10. 5% Pt: (○) 100°C, τ_0 = 50; (△) 160°C, τ_0 = 1.

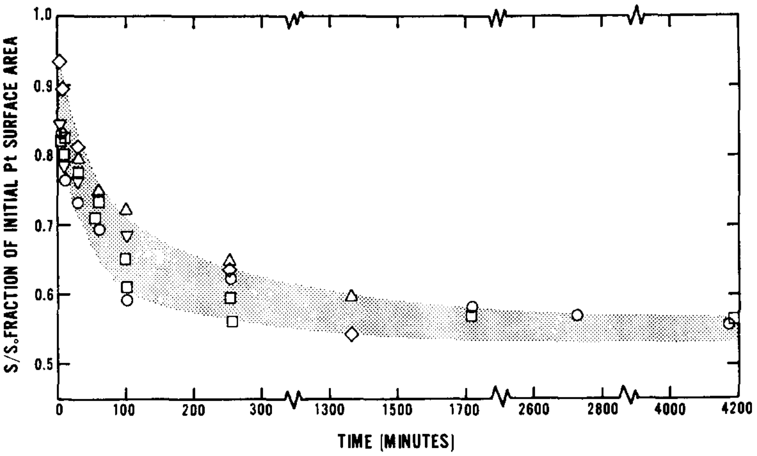

FIG. 3. Influence of potential on Pt crystallite growth for 5% Pt on carbon in 96% H_3PO_4, 160°C. (○) 0.1 V: (□) 0.3 V; (△) 0.5 V; (◇) 0.8 V; (▽) 1.0 V.

data in Fig. 1 indicate no such dependence for liquid-phase sintering of supported Pt electrocatalysts.

The effect of potential on sintering rates of supported Pt is illustrated in Fig. 3. Over a wide potential range, the data appear to fall within the same error limits. It will be argued later that if the mechanism for particle growth required the participation of an electroactive species, for example a platinum ion in solution, such a change in potential would result in a change in the sintering rate of many orders of magnitude. This conclusion is supported by additional experiments which showed that essentially the same rates of particle growth occurred in a number of different solvents of widely varying dielectric constant. These results, listed in Table 1, indicated that although phosphoric acid had the greatest effect, significant loss of Pt crystallite surface area occurred on heating the catalysts in water or toluene. Connolly *et al.* (*10*) had demonstrated previously similar decreases in surface area of supported platinum catalysts in a variety of polar solvents. It is not known, however, whether traces of water in nonpolar solvents are critical to the sintering rates.

TABLE 1

EFFECT OF VARIOUS ENVIRONMENTS ON THE SURFACE AREA LOSS OF PLATINUM ON CARBON AT 100°C

Environment	Pt on Carbon[a] surface area loss (%)		W_{1a} (dyn/cm)
	20% Pt	5% Pt	
Ethylene glycol	11	—	2494
Bromobenzene	12	7	2516
96% H_3PO_4	22	28	2489
H_2O	14	16	2507
Toluene	15	18	2536
Hydrogen	0	0	2574

[a] In 24 hr.

Electron micrographs taken before and after sintering in hot, concentrated H_3PO_4 confirmed that the decrease in platinum surface area was indeed due to Pt crystallite growth. Furthermore, the Pt surface areas calculated from measurements of the Pt crystallite size distributions were in good agreement with the electrochemical surface area measurements.

Typical particle size distributions are shown in Fig. 4 to illustrate the change in the mean Pt crystallite diameter and the broadening of the Pt crystallite size distri-

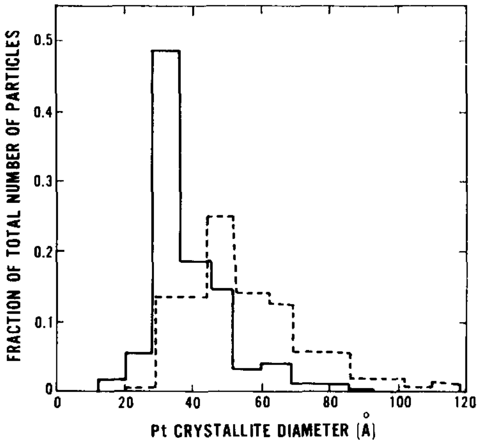

FIG. 4. Effect of crystallite growth on particle size distribution of platinum for 20 wt% Pt on graphitized carbon. (——) initial; (– – –) 1380 min, 0.8 V, 96% H_3PO_4, 160°C.

bution upon sintering in hot, concentrated H_3PO_4. In every case the distribution was determined from a count of more than 500 particles. In view of the limited accuracy with which the Pt crystallite size distribution can be defined and taking into consideration the comments of Flynn *et al.* (*5*) on this problem, no further application of the crystallite size distribution functions was made to interpret the particle growth mechanism.

DISCUSSION

For the majority of conventional chemical reactions, fitting reaction rate data to a given kinetic equation does not constitute a proof of the reaction mechanism. The same comment may be applied to mechanisms for crystal growth of supported metal catalysts where differing conclusions have resulted from different treatments of the same data (*1*, *2*). In order to increase the confidence with which the reaction model may be described, additional mechanistic information is required. For example, comparisons of the Pt crystallite growth for both unsupported Pt and Pt supported on carbon in liquid and gaseous media reveal several instructive similarities and differences. The surface area decreases by unsupported platinum blacks occur in the same temperature range, 100–200°C, and with similar fractional surface area losses, in both liquid and gaseous environments. This is readily established in Fig. 5, by comparing the sintering curves of Kinoshita *et al.* (*11*), of Stonehart and Zucks (*12*), and of McKee (*13*). Furthermore, the apparent activation energy measured in a liquid environment (25 kcal/mole) (*12*) was close to that obtained by Khassan *et al.* (*14*), (18 kcal/mole), in the gas phase. In contrast, Bett *et al.* (*9*) demonstrated that platinum supported on carbon required temperatures in excess of 600°C for significant growth of platinum crystallites in a hydrogen atmosphere, whereas it is shown here that the same catalyst placed in a liquid environment sintered to the same degree at temperatures several hundred degrees lower, comparable to the sintering for unsupported platinum black, and moreover, with an activation energy of similar magnitude, i.e., 21 kcal/mole. These results are summarized in Table 2.

Consideration of these results, may give some indication of the mechanism for crystallite growth of platinum supported on

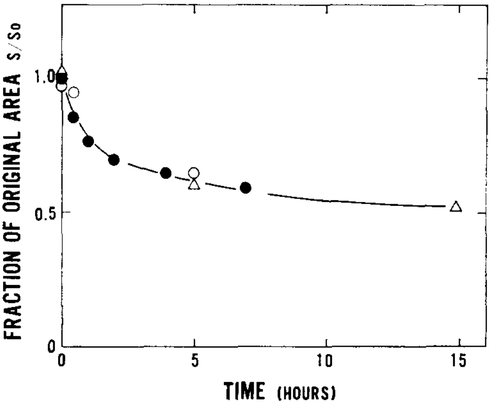

FIG. 5. Comparison of sintering of platinum black at 150°C in gas-phase and in 96% H_3PO_4. (△) Kinoshita *et al.* (*11*), 96% H_3PO_4, 0.5 V; (○) Stonehart and Zucks (*12*); 96% H_3PO_4, 0.5 V; (●) McKee (*13*); reduced, gas-phase.

TABLE 2

Comparison of the Activation Energies for Platinum Crystallite Growth in Liquid and Gas-Phase Environments

Catalyst	Sintering environment	Temp[a] range (°C)	E_a (kcal/mole)
Platinum black	Hydrogen gas	100–200	18 (*14*)
	96% H_3PO_4	100–200	25 (*12*)
Platinum on carbon	Hydrogen gas	600–700	41 (*9*)
	96% H_3PO_4	100–200	21

[a] Temperature range in which surface area loss becomes significant in 24 hr.

carbon in the presence of a liquid phase. For unsupported platinum black it was concluded that mass transport both in gas and in the presence of a liquid phase, occurred by the diffusion of platinum atoms on the platinum crystallite surfaces (*11, 12, 14*). For platinum supported on carbon in a hydrogen gas atmosphere, the loading dependence of the sintering rate indicated that surface migration of platinum crystallites on the carbon was the rate determining process (*9*). Wynblatt and Gjostein (*2*) have recently proposed that this crystallite migration may occur, not by simultaneous translational motion of the whole crystallite body, as suggested by Ruckenstein and Pulvermacher (*1*) and by Masson *et al.* (*18*) but by surface migration of adatoms, on the *metal* crystallite surface, in a random manner with eventual transfer of mass from one side of the crystal to the other, resulting in Brownian motion of the crystal. The effect of liquids in reducing the temperature range for sintering of the supported platinum to the same range as that where the unsupported Pt black sinters suggests the possibility that the role of the liquid might lie in its ability to permit transfer of the platinum adatoms from the platinum surface to the carbon support. In this case surface diffusion of platinum atoms on the carbon surface, i.e., the Ostwald ripening mechanism, would be the mode of mass transfer of Pt from small to larger Pt crystallites.

Consistent with the Ostwald ripening model for particle growth, the experimentally observed rates of sintering for the platinum supported on carbon with a liquid phase present were independent of the metal content. This result follows from the derivation (*4*) of the rate laws for sintering by Ostwald ripening (*2, 4*) in which k, in Eq. (1), is independent of loading, whereas for the crystallite migration model (*1*), k is directly proportional to metal content. Within the Ostwald ripening model, two rate limiting steps are proposed; the surface diffusion of the adatom on the support surface and the interface transfer of the adatom from the support to the metal, or vice versa. For the former step, n has a value of 4 in Eq. (1) and for the latter, n is 3. Wynblatt and Gjostein (*2*) has pointed out that the concept of a nucleation barrier to crystal facet growth, initially applied to explain slow growth rates for bubbles in metals (*19*), may also play a role in the migration processes, producing crystallite growth. Such an inhibition to interface transfer would introduce into the fundamental rate law an exponential term containing the radius of the crystal, i.e.,

$$\frac{dr}{dt} = \frac{k}{r^m} e^{-Ar/RT}. \tag{3}$$

The resulting solution of Eq. (3), cast in the form of Eq. (1), would have an effective exponent, *n*, which increased with time and could reach high values. A value for *n* of approximately 12 was obtained by Wynblatt and Gjostein (*2*) for the sintering of sputtered films of platinum on alumina in low partial pressures of oxygen. In comparison, the value of *n* determined from Fig. 1 was in the range 11–13.

The rate constant, *k*, in the equation for the Ostwald ripening model (*2*) contains a term for the monomer (adatom) concentration on the particle surface, which is in equilibrium with an infinitely large metal crystal. If the adatom species carried significant ionic charge, the concentration would vary by orders of magnitude in the potential range examined in Fig. 3. One must, therefore, infer that the diffusing species is an adatom carrying little ionic charge.

The absence of any effect of potential on the sintering rate also eliminates dissolution and re-deposition of platinum ions for the mechanism of Pt crystallite growth. This conclusion would follow from a consideration of the Pt/Pt^{2+} equilibrium potential at 0.1 V which would require a Pt ion concentration of the order of 10^{-20} moles/liter; a concentration too low to contribute to significant crystallite growth. Even if an allowance was made for increases in solubility of small crystallites as demanded by the Kelvin equation, the Pt ion concentration would still be negligible. An alternative mechanism was also rejected, that is that the rapid initial decrease in Pt surface area might be caused by dissolution of platinum oxide species formed by an oxidation of the smallest platinum crystallites prior to the sintering experiment. This mechanism was excluded by conducting experiments with electrodes which were free of Pt oxide prior to the sintering experiments. The electrodes which were reduced in H_3PO_4 at room temperature were rapidly transferred to the hot phosphoric acid, while being connected continuously to the anode terminal of a potentiostat set at a low potential. The Pt surface area losses measured under these conditions were identical to surface area losses on electrodes which had not undergone the electrochemical reduction step. Finally, no significant platinum loss was observed by chemical analysis of electrodes before and after sintering in hot, concentrated H_3PO_4.

The role of atom diffusion in crystallite growth of supported metals is frequently dismissed on the grounds that the energy difference between the adatom on the substrate and the adatom on the metal surface is large, so the activation energy for an atom transfer process would be prohibitive. (Wynblatt and Gjostein (*2*) reported a value for this energy difference of 100 kcal/mole for Pt on Al_2O_3 in a reducing atmosphere.) Geus (*20*) has pointed out that the presence of defect sites on the support surface can significantly increase the bonding strength of the adatom to the support and thereby reduce the activation energy required for an atom transfer process. Krohn and Barna (*21*) have demonstrated that the presence of hydrocarbon cracking products on rock salt increased the localized metal adatom population. In reviewing the evidence for crystallite motion and atom transfer to the support surface, Flynn and Wanke (*3*) concluded that the latter process can occur to a significant extent on oxide supports above 800°K. It is possible that the highly disordered surface of graphitized carbon black (*15*, *22*) provides sites which are suitable for the surface diffusion of platinum atoms at the lower temperatures of this study. The liquid phase would then serve to facilitate transfer of the metal atom from the Pt crystallite to the support surface.

Crystallite migration has been interpreted as the mechanism to explain sintering of evaporated metal films. Several studies have revealed accelerating effects of water vapor on this process (*20*). When water vapor was adsorbed on a carbon or silicon monoxide substrate and the metal (Ag or Au) evaporated, an enhanced recrystallization was observed, compared to that on the water-free substrate. Even when water was adsorbed *after* evaporation of the metal, recrystallization was enhanced. It was suggested that water molecules were able to penetrate between the metal islands and the substrate to lower the metal/substrate bonding energy and to facilitate migration of the metal crystal. In the present study of platinum on carbon, this effect appears to be minimal since the differences in the work of adhesion for Pt on carbon, calculated in the presence and absence of liquid, were not great. These calculations are summarized in Appendix I and Table 1, together with the Pt area losses in 24 hr, measured in the various liquids. Estimates on the work of adhesion for Pt crystallites to carbon showed little difference between liquid- and gas-phase environments, whereas the experimental Pt surface area losses at 100°C were negligible in the gas phase but 10–20% in the liquid phase. A further argument against crystallite migration as a mechanism for sintering of platinum on graphitized carbon black was provided by the absence of a metal loading dependence for the rate constant. Moreover, if sintering occurred by translational motion of the whole crystallite, it would not be possible to explain the high values of n calculated from Fig. 2. Conversely, if the motion of the crystallites was the result of surface diffusion of platinum atoms on the platinum surface, in the manner proposed by Wynblatt and Gjostein (*2*), a nucleation barrier and large values of n, might be predicted. It would, however, be difficult to explain the accelerating effect of the liquid on the sintering rate for supported platinum, in the absence of a significant effect for the sintering of unsupported platinum black.

Finally, the possibility should be considered that coalescence of the colliding Pt crystallite is rate limiting. According to Ruckenstein and Pulvermacher (*1*), a dependence of the rate constant for sintering on the metal content of the catalyst would again be predicted for this process, which is contrary to the experimental results. Also, large aggregates of coalescing crystallites might be expected to appear in electron micrographs of sintered catalysts if coalescence was the rate determining step, but such aggregates have not been observed.

An evaluation of the evidence bearing on each of the various mechanisms for crystallite growth for platinum supported on graphitized carbon black shows that no single mechanism is without some difficulty in accomodating all of the experimental facts. The data are best explained by an Ostwald ripening process, although more knowledge of the interaction of metal atoms with highly disordered carbon surfaces would be required to substantiate the proposed energy relationships.

APPENDIX I

The Work of Adhesion of Platinum on Carbon

Anticipating that the work of adhesion is related to the interaction energy between Pt crystallites and the carbon substrate, we can obtain estimates of W_a in liquid- and gas-phase environments. The work of adhesion in liquid, W_{la}, is equal to

$$W_{\mathrm{la}} = \gamma_{\mathrm{l\,Pt}} + \gamma_{\mathrm{l\,C}} - \gamma_{\mathrm{Pt\,C}}, \quad \text{(A-I)}$$

where $\gamma_{\mathrm{l\,Pt}}$ and $\gamma_{\mathrm{l\,C}}$ are the surface energies of Pt and carbon in liquids, respectively, and $\gamma_{\mathrm{Pt\,C}}$ is the interfacial energy between Pt and carbon. Similarly, the work of adhesion in air, W_{aa}, is equal to

$$W_{\mathrm{aa}} = \gamma_{\mathrm{a\,Pt}} + \gamma_{\mathrm{a\,C}} - \gamma_{\mathrm{Pt\,C}}. \quad \text{(A-II)}$$

From equilibrium considerations we can relate $\gamma_{\mathrm{l\,Pt}}$ and $\gamma_{\mathrm{l\,C}}$ to contact angles, $\theta_{\mathrm{l\,Pt}}$ and $\theta_{\mathrm{l\,C}}$ at liquid-platinum and liquid-carbon boundaries by Young's equation:

$$\gamma_{l\,\mathrm{Pt}} = \gamma_{a\,\mathrm{Pt}} - \gamma_l \cos \theta_{l\,\mathrm{Pt}}, \quad \text{(A-III)}$$

and

$$\gamma_{l\,\mathrm{C}} = \gamma_{a\,\mathrm{C}} - \gamma_l \cos \theta_{l\,\mathrm{C}}, \quad \text{(A-IV)}$$

where γ_l is the surface tension of the liquid.

Substituting (A-III) and (A-IV) in Eqs. (A-I) and (A-II), respectively, we get

$$W_{la} - W_{aa} = -\gamma_l(\cos \theta_{l\,\mathrm{C}} + \cos \theta_{l\,\mathrm{Pt}}). \quad \text{(A-V)}$$

The terms on the right side represent the reduction in the work of adhesion in the presence of a liquid in comparison with that in air. By choosing liquids with known values of γ_l and with reasonable estimates for contact angles, we were able to calculate the value for the right hand side of Eq. (A-V). It can easily be shown that

$$W_{aa} = \gamma_{a\,\mathrm{Pt}}(1 + \cos \theta_{\mathrm{Pt}}), \quad \text{(A-VI)}$$

where $\cos \theta_{\mathrm{Pt}}$ is the contact angle of Pt on a carbon substrate. Assuming $\theta = 90°$, which has been reported for Pt on Al_2O_3 (*24*), and using $\gamma_{a\,\mathrm{Pt}} = 2574$ dyn/cm (*25*), we can calculate W_{aa} and, therefore, from Eq. (A-V), obtain reasonable estimates for W_{la} in various liquids. These calculations are summarized in Table 1.

REFERENCES

1. Ruckenstein, E., and Pulvermacher, B., *AIChE J.* **19**, 356 (1973); *J. Catal.* **29**, 224 (1973); *J. Catal.* **35**, 115 (1974).
2. Wynblatt, P., and Gjostein, N. A., *Scrip. Met.* **7**, 969 (1973); *Prog. Solid State Phys.* **9**, to be published.
3. Flynn, P., and Wanke, S. E., *J. Catal.* **34**, 390 (1974); *J. Catal.* **34**, 400 (1974).
4. Chakraverty, B. K., *J. Phys. Chem. Solids* **28**, 240 (1967).
5. Flynn, P. C., Wanke, S. E., and Turner, P. S., *J. Catal.* **33**, 233 (1974).
6. Huang, F. H., and Li, C. Y., Scripta Met. **7**, 1239 (1973).
7. Emel'yanova, G. I., and Hassan, S. A., *in* "Proceedings of the 4th International Congress on Catalysis" (J. W. Hightower, Ed. p. 1239. Moscow, 1968.
8. Dunning, W. J., *in* "Particle Growth in Suspensions" (A. L. Smith, Ed.), p. 1. Academic Press, London, 1973.
9. Bett, J. A. S., Kinoshita, K., and Stonehart, P., *J. Catal.* **35**, 307 (1974).
10. Connolly, J. F., Flannery, R. J., and Meyers, B. L., *J. Electrochem.* **114**, 241 (1967).
11. Kinoshita, K., Routsis, K., Bett, J. A. S., and Brooks, C. S., *Electrochim. Acta* **18**, 953 (1973).
12. Stonehart, P., and Zucks, P., *Electrochim. Acta* **17**, 2333 (1972).
13. McKee, D. W., *J. Phys. Chem.* **67**, 841 (1963).
14. Khassan, S. A., Fedorkina, S. G., Emel'yanova, G. I., and Lebedev, V. P., *Zh. Fiz. Khim. SSSR 42*, 2507 (1968).
15. Kinoshita, K., and Bett, J. A. S., *Carbon 11*, 403 (1973).
16. Bett, J. A. S., Kinoshita, K., Routsis, K., and Stonehart, P., *J. Catal.* **29**, 160 (1973).
17. Hoogschagen, J., and Zweitering, P., *J. Chem. Phys.* **21**, 2224 (1953).
18. Masson, A., Metois, J. J., and Kern, R., *Surface Sci.* **27**, 463 (1971); Masson, A., and Metois, J. J., *Surface Sci.* **27**, 483 (1971).
19. Willertz, L. E., and Shewmon, P. G., *Met. Trans.* **1**, 2217 (1970).
20. Geus, J. W., *in* "Chemisorption and Reactions on Metallic Films" (J. R. Anderson, Ed.), Vol. 1, Chap. 3, p. 129. Academic Press, New York, 1971.
21. Krohn, M., and Barna, A., *in* "Proceedings of Second Colloquium on Thin Films, 1967" (E. Hahn, Ed.), p. 45. Van den Hoeck and Ruprecht, Gottingen.
22. Rivin, D., *Rubber Chem. Tech.* **44**, 307 (1971).
23. Phillips, W. B., Desloges, E. A., and Skofronick, J. G., *J. Appl. Phys.* **39**, 3210 (1968).
24. McLean, M., and Hondros, E. D., *J. Mater. Sci.* **6**, 19 (1971).
25. Wasserman, H. J., and Vermaak, J. S., *Surface Sci.* **32**, 168 (1972).