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Redispersion of Platinum Crystallites Supported on Alumina—Role of Wetting

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A thin layer of γ-Al_2O_3 upon which Pt is deposited by evaporation is used to study the redispersion of Pt crystallites supported on alumina. The specimens are subjected to heating in 1 atm O_2, H_2, wet H_2, or wet N_2 at several temperatures and for various lengths of time. The change in size, shape, and position of the Pt crystallites is followed by examining the same region of the same specimen after each step by transmission electron microscopy. Pt crystallites do not redisperse or sinter when heated in O_2 at 750°C and 1 atm. Several cycles of alternating heating of the specimen in O_2 and H_2 at 750°C and 1 atm are needed before Pt crystallites start to redisperse during the oxidation step. Thereafter, redispersion or sintering can be produced periodically by changing the chemical atmosphere from an oxidizing to a reducing one. Heating in wet N_2 has the same effect on redispersion as heating in O_2. Redispersion is caused either by the fracture of the crystallites or by the spreading of platinum oxide over the surface of the substrate. Spreading occurs either because no wetting angle can exist between the oxidized crystallite and substrate, or most probably because a "two-dimensional fluid" of platinum oxide can coexist with the crystallites. Heating in H_2 produces sintering probably because platinum oxide is reduced to Pt which does not wet the substrate. A thermodynamic explanation of the origin of the two-dimensional fluid is provided.

INTRODUCTION

Supported metal catalysts used for high-temperature hydrocarbon processing or auto emission control generally deactivate with time. The deactivation is due among other causes to the agglomeration of the metal crystallites. Rejuvenation by redispersion of the crystallites of the aged catalyst has been reported (*1–10*). Kearby *et al.* (*3*) have shown that crystallites larger than 20 nm of the aged catalyst redisperse to crystallites smaller than 5 nm. The regeneration process generally involves heating the aged catalyst in an oxygen-containing atmosphere such as O_2 or steam, or heating the aged catalyst in an oxygen atmosphere followed by heating in a hydrogen atmosphere. The aged catalysts are sometimes pretreated with chlorine. The conditions and the mechanism or mechanisms by which redispersion of Pt crystallites occurs are not yet clear. Johnson and Keith (*2*) reported redispersion of Pt crystallites in a commercial Pt on alumina catalyst when heated in dry air around 510°C or in 1 atm O_2 around 580°C. Temperatures higher than 580°C caused sintering. Johnson and Keith believe that below

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TABLE 1

Effect of Experimental Conditions on the Average Size of Pt Crystallites Supported on γ-Al_2O_3

Run	Figure	Treatment conditions				Comments
		Atmosphere (1 atm)	Temperature (°C)	Time (hr)	Average size (nm)	
				a	3.3	
1		O_2	750	0–6	3.3	No change
2		O_2	750	6–48	3.3	No change
3		H_2	750	48–54	3.7	Slow sintering
4		H_2	750	54–96	3.9	Slow sintering
5		O_2	750	96–99	4.0	No change
6		H_2	750	99–105	4.2	Slow sintering
7		O_2	750	105–108	4.2	No change
8		H_2	750	108–114	4.3	Slow sintering
9		O_2	750	114–117	4.3	No change
10		H_2	750	117–123	4.5	Slow sintering
11		O_2	750	123–126	4.5	No change
12		H_2	750	126–132	4.6	Slow sintering
13		O_2	750	132–135	4.6	No change
14	1a	H_2	750	135–141	4.6	No change
15	1b	O_2	750	141–144	*b*	Redispersion
16	2a	H_2	850	144–152	15.4	Sintering
17	2b	O_2	750	152–154	*b*	Redispersion
18		O_2	750	154–166	*b*	No change
19	2c	H_2	750	166–167	3.7	Sintering
20		H_2	850	167–168	10.6	Sintering
21		H_2	850	168–169	11.5	Sintering
22		O_2	750	169–170	*b*	Redispersion
23		H_2	550	170–180	*b*	No change
24		H_2	750	180–182	4.7	Sintering
25		H_2	850	182–183	5.7	Sintering
26		Wet H_2	750	183–186	*b*	Redispersion and sintering
27	3a	Wet H_2	750	186–192	*b*	Redispersion and sintering
28	3b	O_2	750	192–194	*b*	Redispersion
29	3c	H_2	750	194–196	4.2	Sintering
30		H_2	850	196–198	13.1	Sintering
31		Wet N_2	750	198–200	*b*	Redispersion
32		H_2	750	200–203	4.1	Sintering

[a] Fresh specimen after heating in H_2 at 750°C and 1 atm for 12 hr.
[b] Most Pt crystallites have sizes smaller than the resolution of TEM.

a critical temperature a Pt–alumina complex existing in an oxidized state is stable and is responsible for redispersion. This critical temperature is near 510°C at 0.2 atm O_2 and near 580°C at 1 atm O_2. Ruckenstein and Pulvermacher (*11*) suggested that redispersion is sometimes caused by the loss of particles to the substrate. Flynn and Wanke (*12*) reported a redispersion in a commercial Pt on alumina catalyst when heated in O_2 around 600°C and 1 atm. They observed sintering at temperatures lower than 500°C or higher than 600°C. Flynn and Wanke explain redispersion as

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a result of the loss of metal oxide molecules from the crystallites to the support.

A direct examination of the changes in size, shape, and position of each crystallite on the support by transmission electron microscopy (TEM) during various stages of treatment can give some insight concerning redispersion. A model catalyst of Pt evaporated on thin films of alumina is suitable for this purpose. Ruckenstein and Malhotra (*10*) carried out such an experiment and observed that redispersion of crystallites occurs when aged specimens were heated at 500°C in air. The purpose of the present paper is to examine the behavior of Pt crystallites of the model catalyst during alternating heating in O_2 and H_2. The present experiments show that no appreciable sintering or redispersion occurs when the specimens are initially heated at 750°C either in pure O_2 or in pure H_2. However, after several cycles of alternating heating in O_2 and H_2 redispersion or sintering start to occur. Thereafter, redispersion and sintering can be produced periodically by changing the chemical atmosphere from an oxidizing to a reducing one. The crystallites redisperse during the oxidizing step and sinter during the reducing step. Heating in wet N_2 has the same effect on redispersion as heating in O_2. When heating has occurred in wet H_2, some crystallites increased in size and others decreased in size, but the behavior of the Pt crystallites appeared to be independent upon size. Redispersion during heating in O_2 and sintering during heating in H_2 are explained below in terms of wetting.

EXPERIMENTAL

Preparation of alumina substrate. Thin films of alumina were prepared by anodization of aluminum foils as described previously (*10, 13*). The anodization solution contained 3% wt tartaric acid with a pH adjusted to 5.5. The voltage was kept at 20 V and the anodization lasted 1 min. This produced a nonporous layer of alumina of about 30 nm thickness on the aluminum foil. After the remaining aluminum foil was dissolved by amalgamation, the thin films of alumina thus obtained were transferred to a large amount of distilled water and picked up on gold grids. They were allowed to dry and were kept in an evacuated dessicator. The alumina films supported on the grid were then heated in a furnace in air at 850°C for 72 hr. During this treatment the amorphous nonporous alumina transformed to γ-Al_2O_3. The substrate did not change its morphology and structure upon further prolonged heating in O_2 or H_2. No reaction between Pt and alumina substrate has been detected by electron diffraction throughout the experiment.

Preparation of Pt supported on alumina substrate. Pt films 1 nm thick were deposited on the alumina substrate by evaporating the corresponding amount of Pt wire in a vacuum unit. Pt wire of 99.999% purity was purchased from Ventron Corporation. The pressure in the vacuum unit during the evaporation was always maintained below 10^{-6} Torr and the substrate was always at room temperature. Electron diffraction has shown that the component evaporated is Pt.

Heat treatment. The heating was carried out in a quartz tube located in a furnace. The temperature of the furnace was controlled to within ±5°C. The specimen introduced in the quartz tube was evacuated by a mechanical pump. After a pressure of 10^{-2} Torr was reached, the mechanical pump was switched off and nitrogen was allowed to flow through the tube at room temperature for 2 hr. The temperature was then raised to the chosen temperature in about 1 to 2.5 hr. As soon as the chosen temperature was reached, N_2 was replaced by H_2 or O_2. The experiments were performed at atmospheric pressure and the flow rate of the gas was 35 cm^3/min. The gases used were all >99.999% purity and were obtained from Linde Division, Union

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Carbide Corporation. Traces of water were removed by passing the gas through 5 A molecular sieves before entering the unit. In the experiments performed in wet N_2 or wet H_2, N_2 or H_2 were respectively passed through a bubbler tube containing H_2O at room temperature before entering the unit. After the desired period of heating, the gas was replaced by N_2 and the quartz tube containing the specimen was cooled to room temperature in about 1.5 hr.

Each specimen was subjected to heat treatment in the following succession:

(i) Thin films of alumina with Pt deposited on them were heated in the quartz tube in flowing H_2 at 750°C and 1 atm for 12 hr. During this treatment, the Pt film broke up and formed Pt islands. The resulting particle size distribution is considered as the initial size distribution.

(ii) The specimen was heated in O_2 at 750°C and 1 atm for 6 to 48 hr.

(iii) The specimen was then heated in H_2 at 750°C and 1 atm for 6 to 48 hr.

(iv) The specimen was subjected to several cycles of alternating heating in oxygen and hydrogen until significant changes were observed in the sizes of the crystallites. Each cycle consisted of heating in O_2 at 750°C and 1 atm for 1 to 3 hr followed by heating in H_2 at the same temperature and pressure for 2 to 6 hr.

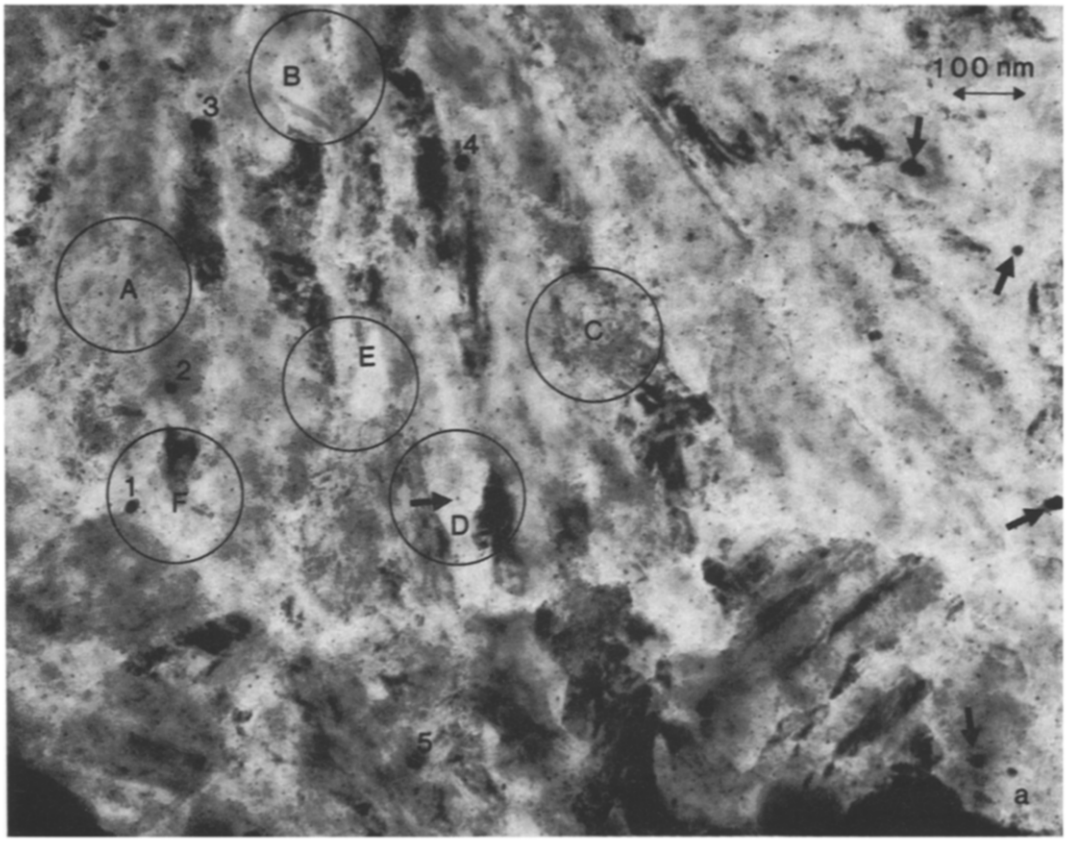

FIG. 1. Transmission electron micrographs showing the same region of a model catalyst. The black particles correspond to Pt and the substrate is γ-Al_2O_3. (a) After five cycles of alternating heating in O_2 and H_2 at 750°C and 1 atm, (b) an additional 3 hr heating in O_2 at 750°C and 1 atm after (a). Most of the Pt crystallites in Fig. 1b are not detected by TEM.

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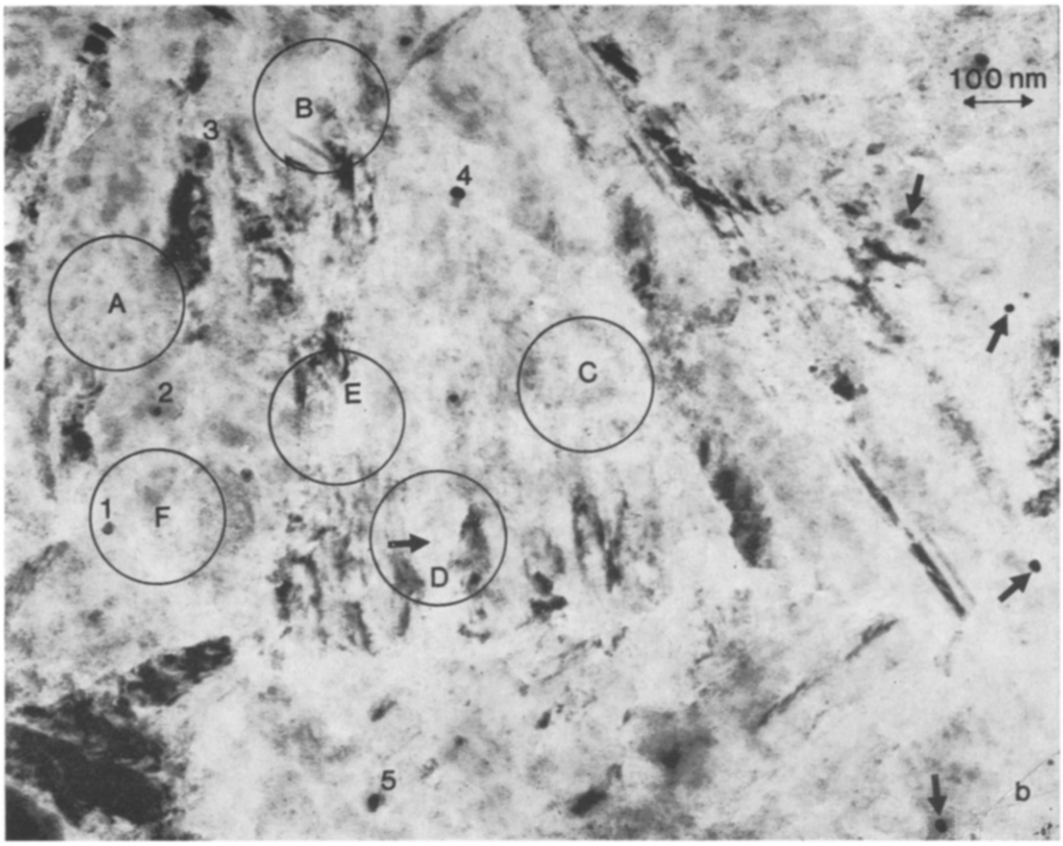

FIG. 1—*Continued.*

(v) The specimen was heated alternatively in O_2 and H_2 at 1 atm and a specified temperature.

By proper rotation, the same regions of the specimen were inspected by TEM after heating so that the change in size, shape, and position of each particle could be detected. The electron microscope has a resolution of about 1 nm. More than 2000 particles were measured on magnified electron micrographs of different regions of at least four specimens which had been heated similarly. The average crystallite size is calculated as $\sum n_i\tilde{D}_i^3/\sum n_i\tilde{D}_i^2$, where n_i is the number of crystallites which have a diameter between D_i and $D_i + \Delta D_i$ and $\tilde{D}_i = D_i + (\Delta D_i/2)$.

Similar final results were obtained when similar specimens were heated continuously for the same total time and exposed only once to air and electron beams for examination in TEM. The effect of contamination due to repetitive contacts with air or exposure to electron beams of the specimens during successive experiments was therefore minimal.

RESULTS

Effect of O_2 and H_2 on the Redispersion

The average size of Pt crystallites after each heating stage is given as a function of time in Table 1. It is clear from runs 1 through 4 in Table 1 that no significant changes in the size of the crystallites occur when the specimen is heated in O_2 for 48 hr followed by heating in H_2 for 48 hr. The average size of the crystallites increased from about 3 to 4 nm. This confirms a

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previous observation (*13*) that pure O_2 or pure H_2 does not appreciably stimulate sintering of Pt crystallites deposited by evaporation on thin films of γ-Al_2O_3. No redispersion of Pt crystallites occurred during this treatment. [It should be noted that, in contrast to the model catalyst used here, appreciable sintering of the crystallites occurs when industrial catalysts are heated in O_2 at high temperature (*6, 8, 9, 12*). The difference in the method of preparation and the nature of the substrate probably explains the different behaviors.]

The specimens were then heated alternatively in O_2 or H_2 for five cycles at 750°C and 1 atm (runs 5 through 14, Table 1). The five cycles of heating caused a small increase in the average size of the Pt crystallites from about 4 to 5 nm. The electron micrograph of Fig. 1a shows the morphology of Pt on the alumina substrate after run 14. The black particles are Pt and the substrate is γ-Al_2O_3. The grain boundaries of γ-Al_2O_3 are readily observed. After the specimen was heated in O_2 at 750°C and 1 atm for 3 hr (run 15, Table 1) the crystallites decreased in size (Fig. 1b). Furthermore, most of the crystallites from Fig. 1a can no longer be detected in Fig. 1b. Compare, for example, regions A through F and those crystallites marked by numbers

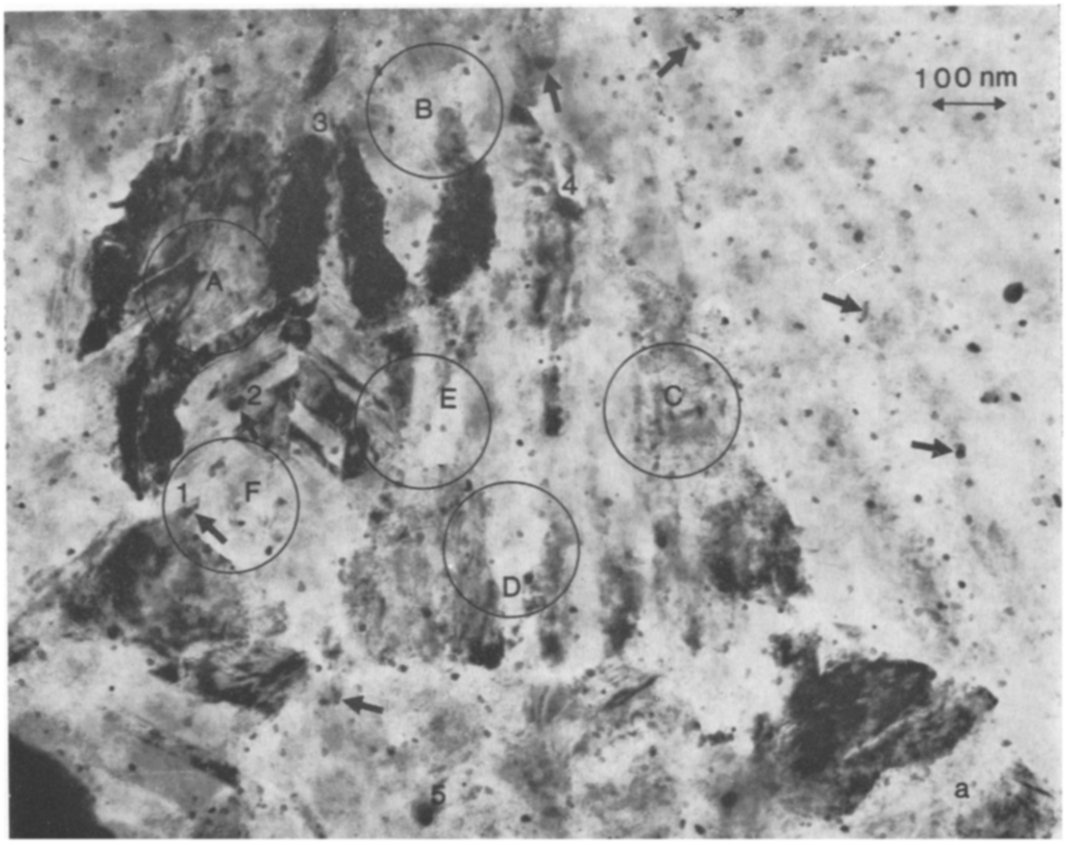

FIG. 2. Transmission electron micrograph showing the same region of the model catalyst. (a) An additional 8 hr of heating in H_2 at 850°C and 1 atm after 1b. Pt crystallites sinter and grow in size. (b) An additional 2 hr heating in O_2 at 750°C and 1 atm after 2a. Redispersion of Pt crystallites occurs. (c) An additional 12 hr of heating in O_2 and 1 hr heating in H_2 at 750°C and 1 atm after 2b. Pt crystallites sinter and reappear.

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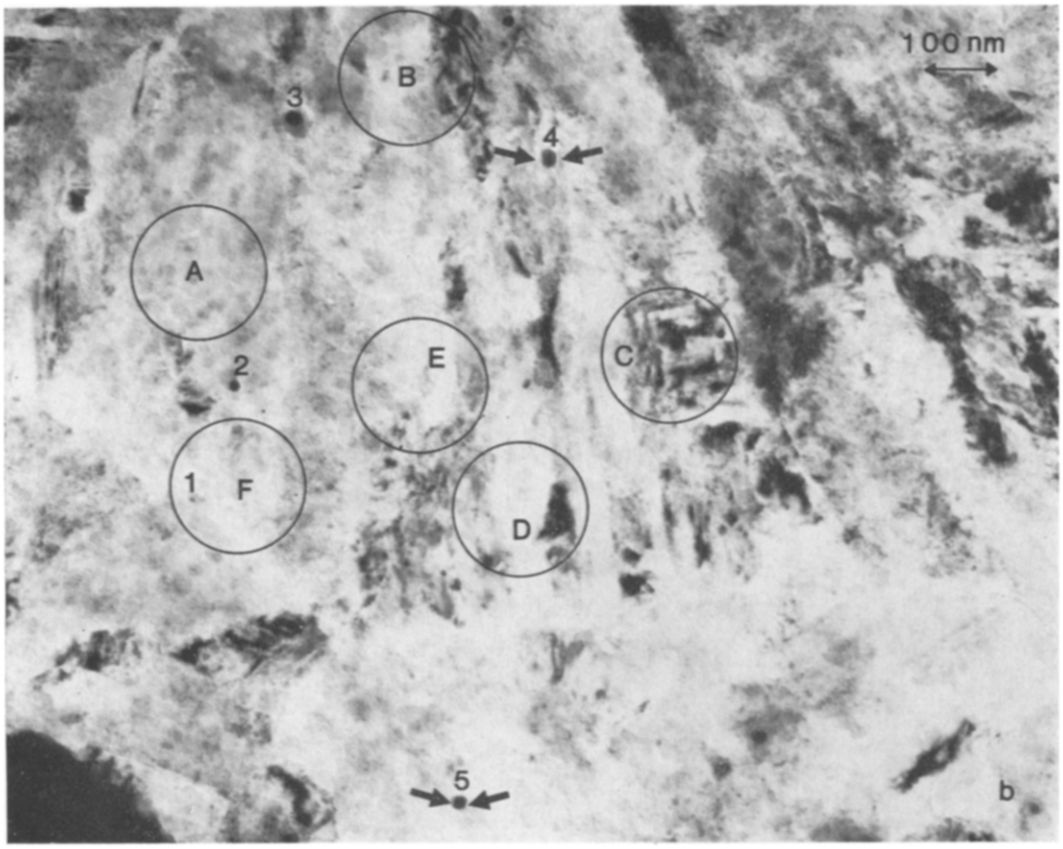

FIG. 2—*Continued.*

or arrows of both Figs. 1a and b. The undetected crystallites did not evaporate from the specimen since, as will be shown later, Pt reappears during heating in H_2 (see Fig. 2a). The crystallites were not detected by TEM because the initial crystallites redispersed as particles with sizes smaller than the resolution of TEM. As explained below, platinum is probably oxidized to platinum oxide which better wets the substrate. Chu and Ruckenstein have provided evidence by electron diffraction that platinum is oxidized in an oxygen atmosphere (*14*).

The specimen of Fig. 1b was further heated in flowing H_2 at 850°C and 1 atm for 8 hr. The Pt crystallites reappeared and grew to an average size of about 15 nm (run 16, Table 1). They are relatively thin but have clear boundaries and irregular shapes on the substrate (see Fig. 2a). The dumbell-shape morphology of some Pt crystallites shown by arrows in Fig. 2a gives indication that migration and coalescence occurred.

After several cycles of alternating heating in O_2 and H_2 (runs 5 though 14, Table 1), redispersion or sintering could be produced periodically by heating in O_2 or H_2, respectively. Similar results were obtained on at least four specimens. The electron micrographs shown in the present paper are taken from the same region of one of the specimens.

Redispersion and Sintering of Pt Crystallites

The specimen of Fig. 2a was further heated in O_2 at 750°C and 1 atm for 2 hr.

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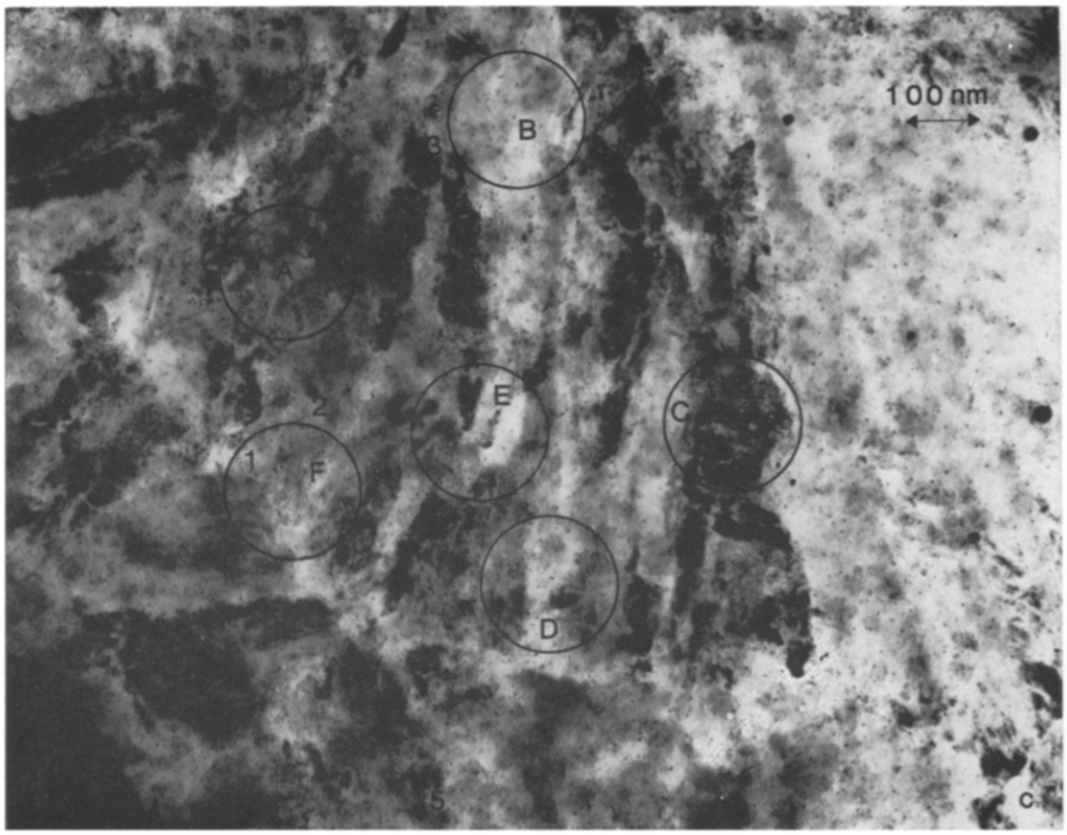

FIG. 2—*Continued.*

Significant changes occur (see Fig. 2b). Comparing, for example, regions A to F in Figs. 2a and b, one can observe that most of the crystallites in Fig. 2a no longer appear in Fig. 2b. Again, Pt did not disappear from the specimen since it reappears as crystallites when heated in H_2 (Fig. 2c). The large crystallites 1 to 5 in Fig. 2a decrease in size during heating in O_2 (Fig. 2b). They also change their shapes. It may be noticed that crystallite 4 and 5 have smooth boundaries in Fig. 2a but sharp edges (indicated by arrows) in Fig. 2b. We intended to redisperse the remaining large crystallites further by additional heating in O_2 for 12 hr (run 18, Table1). However, no significant change could be detected on the specimen. The small crystallites and/or the metal-oxide molecules undetected by TEM in Fig. 2b sintered and grew in size during heating in H_2 at 750°C and 1 atm for 1 hr (run 19, Table 1). A large number of small crystallites of about 4 nm appears (Fig. 2c). Regions A to F of Fig. 2 show the same regions of the specimen. It can be seen that most of the crystallites in Fig. 2c are new crystallites occupying positions where no crystallites were detected previously in Figs. 2a and b. Almost all the crystallites of Fig. 2c are of about 4 nm size, hence they are much smaller than the crystallites of Fig. 2a which are of about 15 nm size. The number of Pt crystallites observed in Fig. 2c is at least 25 times larger than that in Fig. 2a. The alternating heating in O_2 and H_2 was continued several times (Table 1). Redispersion occurred when the specimen was

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heated in O_2, and sintering occurred when the specimen was heated in H_2.

Effect of Wet H_2 or Wet N_2 on Redispersion

After alternating heating in O_2 and H_2 the specimen was further heated in wet H_2 at 750°C and 1 atm for 3 hr (run 26, Table 1). Some crystallites increased in size and others decreased in size. However, their behavior appeared to be independent of size. In addition it was found that redispersion of the Pt crystallites occurs during heating in wet N_2.

DISCUSSION

Two mechanisms appear to explain the redispersion observed in our experiments: (a) fracture of crystallites, and (b) spreading of platinum oxide (formed in the oxidizing atmosphere) over the surface of the substrate.

Redispersion by Fracture

Crystallites 6, 7, and 8 of about 40 nm size in Fig. 3a are fractured into smaller particles in Fig. 3b. The crystallites resulting through fracture sintered after heating in H_2 (Fig. 3c). This fracture can be explained in terms of the stability theory developed by Ruckenstein and Dunn (*15*). Let us consider a thin film on a substrate and apply a small, spatially periodic displacement to its free interface. If the response of the system increases the effect of the perturbation, then the film may fracture. In the converse case the film is stable. The response of the system is determined by the surface diffusion of the atoms, which, in turn, is generated by a gradient of the chemical potential along the perturbed free interface of the film. The chemical potential is expressed in terms of the curvature of the interface, of the preexisting internal stresses in the film, and of the interaction forces between the metal atoms at the gas–solid interface and those of the film and substrate. The latter interactions have to be taken into account when the range of the interaction forces between one atom of the film and the entire substrate is larger than the thickness of the film. Surface diffusion can amplify, under some conditions, the initial perturbation leading to fracture. The calculations predict a critical prestress required for fracture which decreases as the surface tension decreases. The theoretical considerations (*15*) are valid for thin films and can probably be extended only to sufficiently large crystallites. In the case of small crystallites, their shape and size are expected to affect stability.

Oxidation of platinum to platinum oxide generates an internal stress and decreases the film-gas surface tension. Fracture occurs when the internal stress is larger than the critical stress. Rapid cooling also generates internal stresses because of differences in the thermal expansion coefficients of the metal and substrate, and these can induce fracture. This kind of behavior was observed in references 10 and 14.

Redispersion by Spreading

Two kinds of spreading are distinguished here. In the first kind, no wetting angle can exist between crystallites and substrate; in the second kind a wetting angle is possible, but a two-dimensional fluid coexists with the crystallites. The thermodynamic origin of the two-dimensional fluid is examined at the end of this section.

For a crystallite in thermodynamic equilibrium on the substrate, the three surface tensions are related through Young's equation (Fig. 4)

$$\sigma_{gs} - \sigma_{ms} = \sigma_{mg} \cos \theta, \qquad (1)$$

where σ is the surface tension (the subscripts gs, ms, and mg refer to the gas–substrate, metal–substrate, and metal–gas interfaces, respectively) and θ is the wetting angle. For very small crystallites the

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equilibrium problem is more complicated and has to be examined along the lines developed by Ruckenstein and Lee (*16*). For the sake of simplicity and because the present discussion is largely qualitative, Young's equation is used as the starting point.

In vacuum, the metals have high surface tensions. For instance, Pt has a surface tension of 2340 erg cm^{-2} at 1310°C; for Ni at 1250°C it is 1850 erg cm^{-2} (*17*). The oxides have a surface tension lower than that of the metals. [Since no values are available for platinum oxide, we mention that the surface tension of Ag at 932°C is a function of the partial pressure of oxygen, decreasing from about 1100 erg cm^{-2} at 10^{-6} atm to about 300 erg cm^{-2} at 1 atm (*18*)]. For this reason the metals do not wet the oxides. However, if the metal is oxidized, its surface tension decreases appreciably. If the entire crystallite is oxidized, the crystallite-substrate interfacial tension is also expected to decrease. In these conditions it is possible to have

$$\sigma_{gs} - \sigma_{ms} > \sigma_{mg}. \qquad (2)$$

No wetting angle is, however, compatible with inequality (2), which leads to $\cos\theta > 1$, and therefore the crystallite has to spread over the entire surface available (*11*), ultimately as single molecules. When platinum oxide is reduced by heating in H_2, the crystallites form once again since platinum does not wet alumina and hence $|\sigma_{gs} - \sigma_{ms}| < \sigma_{mg}$.

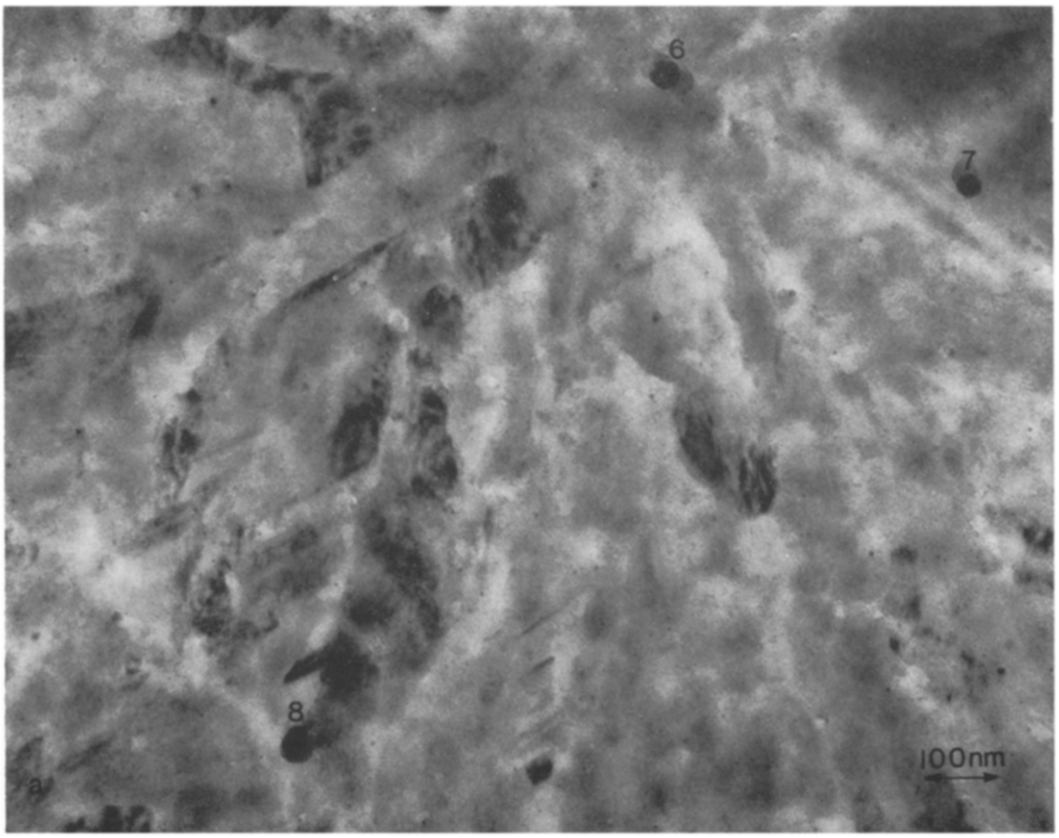

FIG. 3. Transmission electron micrographs showing the same region of the model catalyst (a) after run 27 (Table 1); (b) an additional 2 hr of heating in O_2 at 750°C and 1 atm after 3a; (c) an additional 2 hr of heating in H_2 at 750°C and 1 atm after 3b.

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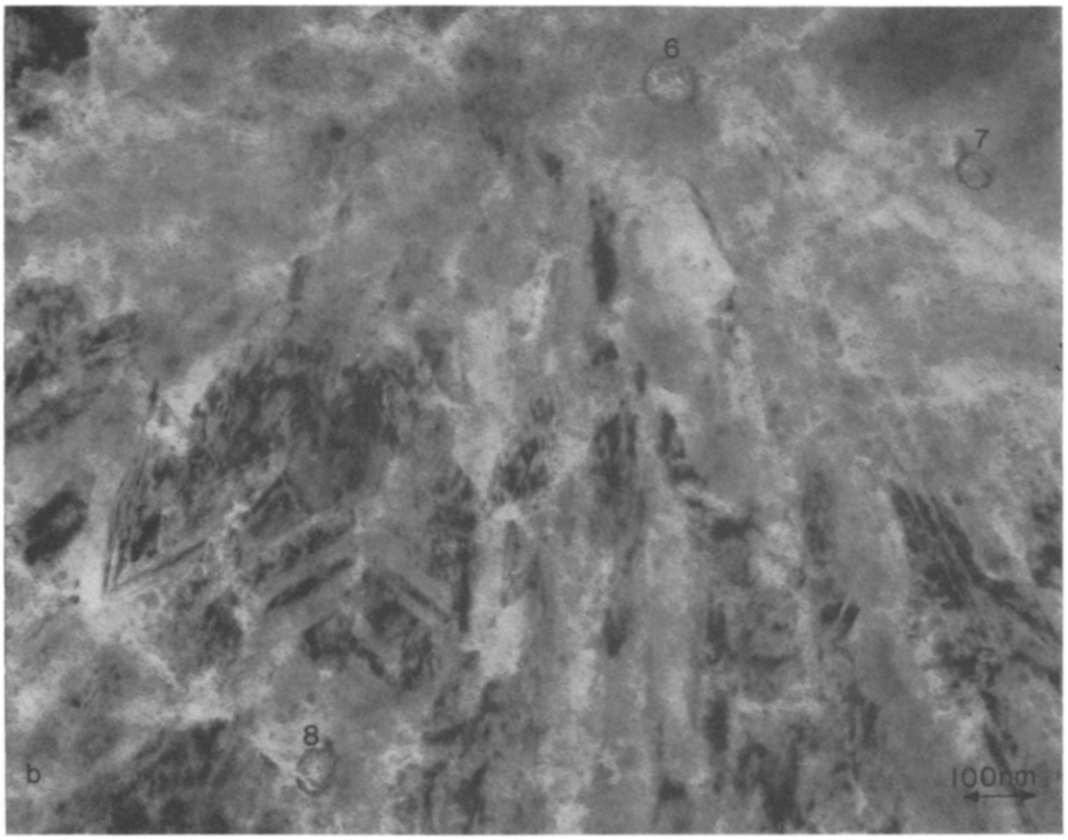

FIG. 3—*Continued.*

The first five or six cycles of heating in O_2 and H_2 probably generate some porosity in the crystallites and, in this manner, enhance the oxidation of the smaller crystallites. They also produce some reconstruction of the substrate. Only after this initial process condition (2) is satisfied and can redispersion occur. The large crystallites are oxidized completely only near their leading edge where they are sufficiently thin. Therefore, only that part of the larger crystallites spreads as molecules of platinum oxide over the substrate. The remaining part which does not spread is constituted of pure metal protected by an oxide layer. The sharp edges of the larger crystallites, observed in our experiments after redispersion during heating in O_2 (Fig. 2b), may be due to this process.

In the kind of spreading just discussed, no wetting angle can exist between crystallites and substrate. However, another kind of wetting can also explain the observed phenomena. In this case crystallites coexist with a thin layer of platinum oxide which can be a two-dimensional fluid, a bilayer, or a multilayer. In the present experiments one starts with platinum metal which, for reasons already mentioned, does not wet the substrate. A part of the platinum oxide formed during heating in oxygen will spread through the leading edge of the crystallite to wet the substrate as a two-dimensional fluid of molecules of platinum oxide. Reducing platinum oxide to Pt which does not wet the substrate, the two-dimensional fluid recondenses into metal crystallites,

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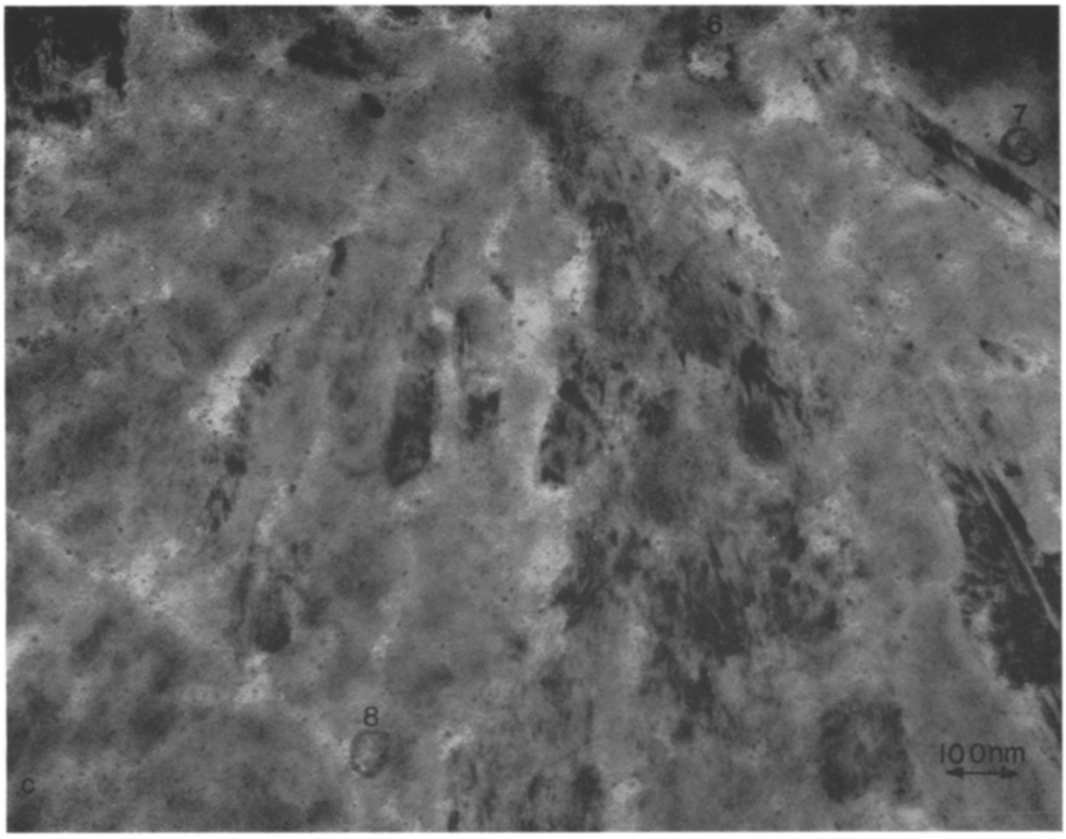

FIG. 3—*Continued.*

being either recaptured by the remaining crystallites or forming new ones.

It is interesting to observe that even in the second kind of wetting, platinum oxide crystallites smaller than a critical size have the tendency to wet the substrate completely. This is due to a Kelvin-type effect which generates in the smaller crystallites a higher dissolution surface pressure than in the larger ones. This dissolution surface pressure has to be added to σ_{gs} and, as long as the radius of the crystallite is small enough, can lead to the inversion of the inequality $\sigma_{gs} - \sigma_{ms} < \sigma_{mg}$ and hence to spreading (see also Appendix A).

A thermodynamic explanation of the origin of the two-dimensional fluid was provided in Ref. (*19*) using as a starting point the specific free energy of formation σ of a thin film on a substrate. If the film is thick, σ is given by the expression

$$\sigma(\infty) \equiv \sigma_\infty = \sigma_{mg} + \sigma_{ms} - \sigma_{gs}. \quad (3)$$

Spreading occurs if $\sigma_\infty < 0$. As soon as the range of the interaction forces between one atom of the film and the substrate becomes larger than the thickness of the film, the film can no longer be assumed macroscopic and the specific free energy of formation σ becomes a function of the thickness h of the film

$$\sigma(h) = \sigma_\infty + f(h), \quad (4)$$

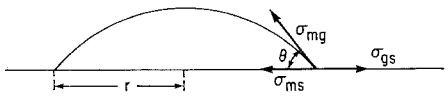

FIG. 4. Droplet on a substrate.

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where $f(h) \to 0$ when $h \to \infty$. If a Lenard–Jones potential is used for the interaction potential the following approximate expression is obtained for $f(h)$ (*19*):

$$f(h) = \frac{\alpha}{h^2} - \frac{\beta}{h^8}, \tag{5}$$

where α and β are constants. If $\sigma(h)$ is always negative, spreading occurs for all possible loadings of the substrate, whereas if $\sigma(h)$ is always positive no spreading occurs. When, however, $\sigma_\infty > 0$ but $\sigma(h) < 0$ for $h < h_0 \ll \infty$, then a thin film (probably a submonolayer) may coexist with the crystallites. A detailed examination of the problem with its implications for both sintering and redispersion is presented in Ref. (*19*).

CONCLUDING REMARKS

Several cycles of alternating heating in O_2 and H_2 at 750°C and 1 atm are needed before redispersion of Pt crystallites occurs. After these cycles of treatment, redispersion and sintering can be produced periodically by changing the chemical atmosphere from an oxidizing to a reducing one. Crystallites redisperse during the oxidation step and sinter during the reduction step. Wet N_2 has the same effect as O_2 as concerns the redispersion of Pt model catalyst. Redispersion is caused in an oxygen atmosphere by spreading of platinum oxide over the surface of the substrate. Spreading occurs either because no wetting angle can exist between the oxidized crystallites and substrate or, most probably, because a two-dimensional fluid of platinum oxide can coexist with the crystallites. There are conditions under which splitting of large crystallites can also occur. Sintering occurs during heating in H_2 because the oxide is reduced to metal and the metal does not wet the substrate. A thermodynamic explanation of the origin of the two-dimensional fluid is provided.

APPENDIX A

Following the procedure used to derive an equation for the effect of curvature on the vapor pressure, one obtains for the dissolution surface pressure p_s

$$p_s = p_{s\infty} \exp\frac{\delta}{r} \tag{A1}$$

where

$$\delta \equiv \sigma_e S_e / kT, \tag{A2}$$

$p_{s\infty}$ is the dissolution surface pressure for large crystallites, r is the radius of the crystallite–substrate interface, S_e is the surface area per molecule at the crystallite–substrate interface, k is Boltzmann's constant, T is the absolute temperature, and σ_e is the line tension in erg cm^{-1} at the leading edge of the crystallite. Further, denoting by $n_{s\infty}$ the number of molecules of platinum oxide per unit area of substrate in equilibrium with the large crystallites and assuming a two-dimensional ideal gas (although a two-dimensional van der Waals fluid is a more adequate assumption), one can write

$$p_{s\infty} = n_{s\infty} kT. \tag{A3}$$

Near the leading edge of the crystallite, on the substrate, there are at a given moment n molecules per cm^2. These molecules of platinum oxide generate a surface pressure nkT which opposes wetting.

Hence one can find a critical radius r_c below which spreading is possible from the equality

$$\sigma_{gs} + \left[n_{s\infty}\left(\exp\frac{\delta}{r_c}\right) - n \right] kT - \sigma_{ms} = \sigma_{mg}. \tag{A4}$$

Of course, only if the detachment of molecules during spreading maintains $r < r_c$

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will spreading continue. Equation (A4) leads to

$$\frac{r_c}{\delta} = \left[\ln \frac{\sigma_{mg} + \sigma_{ms} - \sigma_{gs} + nkT}{n_{s\infty}kT}\right]^{-1}. \quad \text{(A5)}$$

Detachment of molecules will occur if the area concentration of molecules in equilibrium with a crystallite of radius r, $n_{s\infty} \exp(\delta/r)$, is larger than n. Because the surface tensions are of the order of a few hundred erg cm^{-2}, taking $\sigma_{mg} + \sigma_{ms} - \sigma_{gs} + nkT \approx 10^2$ erg cm^{-2} and $kT = 1.3 \times 10^{-13}$ erg, a relatively large value of $n_{s\infty} = 7 \times 10^{14}$ cm^{-2} is needed to obtain $r_c/\delta \approx 10$. No values are available for the line tension. Assuming $\delta \approx 10^{-7}$ cm results in a value of r_c of the order of 10^{-6} cm.

To be consistent the contribution σ_e/r_c of the line tension should be substracted from the left hand side of Eq. (A4). This contribution is negligible for sufficiently large radii, but becomes important when the radius is sufficiently small. However, as already mentioned, Young's equation (corrected to include the contribution of the line tension) and, hence, Eq. (A4) are no longer valid for sufficiently small radii [16].

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