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On the Sintering of Platinum on Alumina Model Catalyst

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A model catalyst suitable for examination in the transmission electron microscope is used to study the sintering of Pt crystallites supported on alumina. The model catalyst consists of a thin layer of γ-Al_2O_3 upon which Pt is deposited. The samples are subjected to heating in various chemical atmospheres for various lengths of time and temperatures. The change in size, shape, and position of each Pt crystallite is followed by examining the same region after each step in the treatment. Crystallite migration is identified as a cause of sintering. Evidence for the migration of crystallites of size larger than about 10 nm over large distances is presented. The degree of mobility of Pt crystallites depends on sintering conditions. Increase in temperature, periodic oxidation and reduction, reaction of Pt with the substrate, and burning off of coke accumulated on the surface all enhance crystallite migration. Phase transformation occurring in the alumina substrate is also associated with severe sintering of Pt crystallites. Heating of the model catalyst in pure oxygen or wet N_2 does not promote Pt sintering appreciably. Significant sintering occurs during heating in wet H_2.

INTRODUCTION

Pt catalysts supported on alumina deactivate during the catalytic process or during prolonged exposure to high temperature. An important cause of catalyst deactivation is the sintering of the dispersed crystallites. Recently, Dalla Betta *et al.* (*1*) compared the relative importance of sintering and chemical poisoning of supported noble metal automotive oxidation catalysts. They found that sintering of the catalyst accounted for a 20-fold drop in the available noble metal area while poisoning decreased the area by a further factor of 20. Two basic mechanisms of sintering have been suggested. Ruckenstein and Pulvermacher (*2, 3*) assume migration and coalescence of the dispersed metal crystallites on the support. Although the larger crystallites have a very low mobility, they grow in size through the migration of the smaller crystallites which collide and coalescence with the larger ones. Wynblatt and Gjostein (*4*) and Flynn and Wanke (*5, 6*) assume that single atoms are the only mobile particles. The small crystallites decrease in size by losing atoms while the larger ones increase in size by gaining atoms (Ostwald ripening mechanism). Recently, Ruckenstein and Dadyburjor (*7*) developed a more complete treatment of the Ostwald ripening which they combined with the crystallite migration and coalescence model (*2, 3*). The new model provides a treatment accounting for migration and coalescence as well as for emission of particles.

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The sintering of Pt crystallites supported on alumina has been experimentally examined under various conditions (*8–12*). However, few experiments performed have been able to identify the mechanism of sintering (*13–15*). Baker *et al.* (*14*) using controlled atmosphere electron microscopy (CAEM) followed continuously the behavior of Pt on alumina in 2 Torr O_2 or N_2. The temperature was gradually raised in about 1 hr to 500, 800, and above 900°C. They found, among others, that the large particles are immobile and that the growth of the particles probably occurred via the movement of particles of less than 2.5 nm diameter. The total time of heating was, however, about 1 hr. In a previous paper (*15*) we have studied the sintering behavior of Pt on carbon substrates. The specimen was heated outside the electron microscope in various chemical atmospheres, but the same region of the same specimen was examined after each treatment. Crystallite migration and coalescence were found to be responsible for the sintering observed. A significant migration of crystallites larger than 20 nm diameter took place even at very low pressures of oxygen. The migration of crystallites is caused mainly by the gas produced during the catalytic combustion of the carbon substrate. However, this mechanism is not applicable to the Pt–alumina system because alumina is in a large measure inert to the chemical atmospheres.

It is the purpose of the present work to obtain information about the mechanism of sintering of Pt crystallites on alumina substrates. A model catalyst suitable for examination in TEM is used. The catalyst consists of a thin layer of alumina film upon which Pt crystallites are deposited. The specimen was heated outside the electron microscope, but nearly the same region of the same specimen was examined after each treatment. This technique creates some difficulties in locating with precision, in successive observations, the same region at the same rotation. It offers, however, the advantage that TEM has a higher resolution than CAEM. In the present work, the sintering behavior is studied as a function of temperature, time, and chemical atmosphere. The effects on sintering of Pt crystallites of the phase transformations in alumina, of the reaction of Pt with alumina, and of the burning off of the coke accumulated on the surface are also examined. It is shown below that crystallite migration and coalescence are responsible at least in part for sintering. The degree of mobility of Pt crystallites depends on the sintering conditions.

EXPERIMENTAL

Preparation of alumina substrate. Thin films of alumina were prepared by anodic oxidation of aluminum foils. The detailed anodization procedure has been given in previous papers (*16*, *17*). The anodization solution contained 3 wt% tartaric acid adjusted with ammonium hydroxide to a pH of 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. The aluminum foil together with the alumina film was cut into small squares and floated on a dilute mercuric chloride solution. After the aluminum foil was dissolved the alumina films were floated off from the solution. The films were then transferred to large amounts of distilled water and picked up on electron microscope grids, allowed to dry, and kept in an evacuated desiccator. The electron microscope grids used depended on the conditions required. When the samples were heated in air, gold grids were used to avoid the oxidation of the grids. If heating occurred in a high vacuum unit, tungsten grids replaced the gold ones to avoid the evaporation of gold. Experiments show that the nature of the grid does not affect the sintering process. The alumina films supported on the grid were then heated in a furnace in air at 800°C for 72 hr. This treatment transformed the amorphous nonporous alumina completely to γ-Al_2O_3. The substrate did not change further its morphology during further experiments. The heat treatment of alumina before Pt is deposited is absolutely necessary, because as it will be shown below, phase transformation of alumina causes severe sintering of Pt. After heating, the substrate was cooled in air to room temperature and stored in an evacuated desiccator to avoid contamination before deposition of Pt.

Preparation of Pt supported on alumina substrate. A Pt film of about 2 nm thickness was 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 Corp. The pressure in the vacuum unit during the evaporation was always maintained below 10^{-6} Torr, and the substrate was always at room temperature. To be sure that the component evaporated is Pt, two test carbon substrates were introduced together with the alumina substrates in the vacuum unit. The electron diffraction of the specimen supported on carbon invariably indicated Pt.

Heat treatment. Heat treatment was carried out either inside a vacuum unit or in a quartz tube. For pressures less than 10^{-4} Torr heating took place in the vacuum unit. This kind of heating was used to transform γ-Al_2O_3 to α-Al_2O_3 to study the effect of substrate phase transformation on sintering. A tantalum boat was used as the heater. The temperature was controlled to within ±5°C. The unit with the specimen inside was evacuated to 10^{-6} Torr and then heated to the chosen temperature in 0.5 to 1 hr. As soon as the temperature reached 850°C, either vacuum was maintained or H_2 gas was passed through the unit. After heat treatment for the desired period of time, the current to the heater was cut off, and the specimen was cooled under vacuum conditions. Temperatures dropped off very rapidly, reaching 40°C in about 5 min and room temperature in about 30 min.

Experiments at atmospheric pressure were performed in a quartz tube heated in a furnace. The specimens were introduced in the quartz tube and 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 furnace 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, O_2, or the desired mixtures of gases. The flow rate of the gases was 35 ml/min. The gases used were all of $>99.999\%$ purity and were obtained from Linde Division, Union Carbide Corp. Traces of water were removed by passing the gas through 5A molecular sieves before entering the unit. In the experiments performed in wet N_2 or wet H_2 atmosphere, N_2 or H_2 were first passed through a bubbler tube containing H_2O at room temperature before entering the unit. After heat treatment for the desired period of time, the gas was replaced by N_2, and the furnace was cooled to room temperature in about 1.5 hr.

The specimens were heat-treated according to the following steps:

1. Thin films of alumina with Pt deposited on them were heated in the quartz tube in flowing H_2 at 500 or 750°C and 1 atm for 6 hr. By this treatment, the Pt film broke up and formed Pt islands. The resulting particle size distribution is considered as the initial particle distribution.
2. The specimens were then heated at the same temperature (500 or 750°C) in various chemical atmospheres for an interval of 6 to 48 hr.
3. The temperatures of the specimens were raised from 500 to 650°C or from 750 to 850°C in the same chemical atmospheres and heated for various time periods.

The same region of a specimen was

TABLE 1

Effect of Experimental Conditions on the Sintering of Pt Crystallites Supported on γ-Al_2O_3 Substrate

Treatment conditions		Time (hr)	Average size (nm)
Atmosphere	Temperature (°C)		
Vacuum, 1×10^{-6} Torr	500	$t = 0$	5.5
	500	$t = 48$	5.9
	500–650[a]	Additional 1 hr	6.6
	650	Additional 6 hr	7.0
	650	Additional 24 hr	7.3
H_2, 1 atm or N_2, 1 atm	500	$t = 0$	5.5
	500	$t = 48$	6.0
	500–650[a]	Additional 1 hr	6.6
	650	Additional 6 hr	7.1
	650	Additional 24 hr	7.4
	750	$t = 0$	8.5
	750	$t = 48$	9.0
	750–850[a]	Additional 1 hr	9.6
	850	Additional 24 hr	9.9
20% O_2 in N_2, 1 atm or O_2, 1 atm or wet N_2, 1 atm	500	$t = 0$	5.5
	500	$t = 48$	5.7
	500–650[a]	Additional 1 hr	6.4
	650	Additional 24 hr	6.7
	750	$t = 0$	8.5
	750	$t = 48$	8.9
	750–850[a]	Additional 1 hr	9.4
	850	Additional 24 hr	9.5
Wet H_2, 1 atm	500	$t = 0$	5.5
	500	$t = 6$	9.0
	500–650[a]	Additional 1 hr	11.4
	650	Additional 3 hr	16.2

[a] Intermediate heating stage.

followed several times. The change in size, shape, and position of each particle could thus be detected after each heating. The particle size distribution was measured by following many regions of the same specimen or different specimens which had been treated similarly.

To determine the effect of contamination because of repetitive contacts with air during successive experiments, identical specimens were heated continuously for the same total time and exposed only once to air for examination in TEM. No significant difference could be detected between the two electron micrographs taken at the end of the experiments. It seems, therefore, that there was a minimal effect of contamination by air.

EXPERIMENTAL RESULTS AND DISCUSSION

The average size of Pt crystallites heated in different chemical atmospheres at various temperatures is given as a function of time

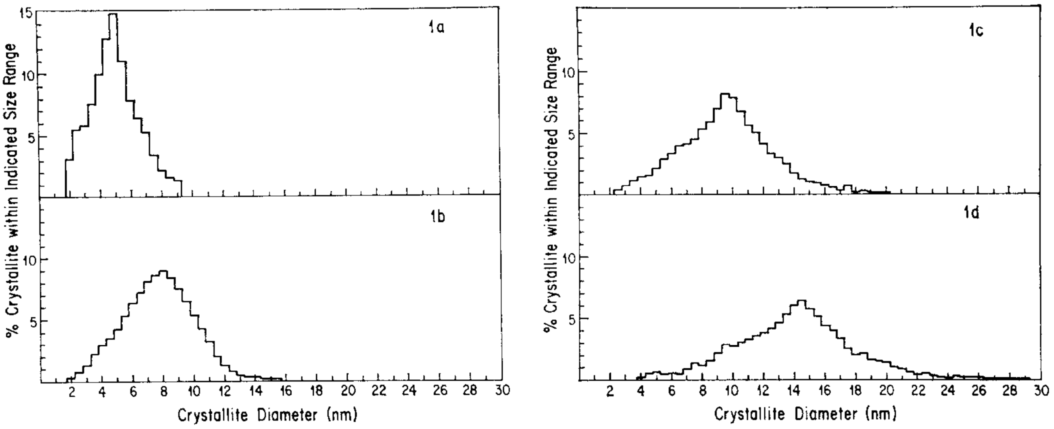


FIG. 1. Size distribution of Pt crystallites: (a) fresh specimen; (b) specimen heated at 500°C for 6 hr; (c) specimen further heated at 650°C for 1 hr; (d) additional heating at 650°C for 3 hr.

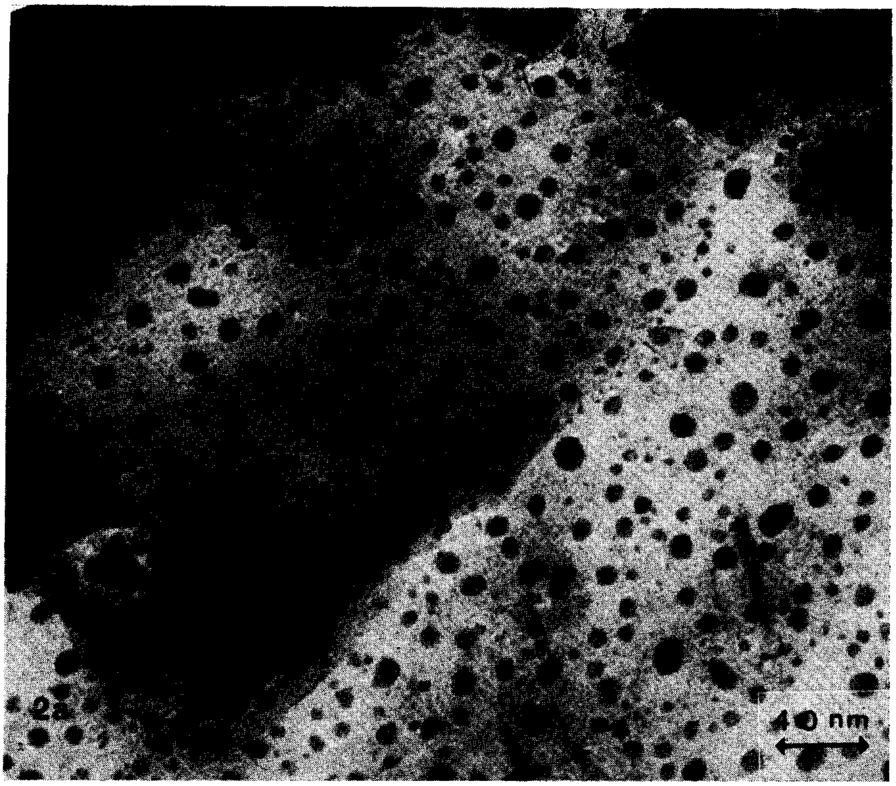
in Table 1. The average crystallite size is calculated as $(\Sigma n_i \tilde{D}_i^3 / \Sigma n_i \tilde{D}_i^2)$, where n_i is the number of crystallites which have a diameter between D_i and $D_i + \Delta D_i$, $\tilde{D}_i = D_i + (\Delta D_i/2)$. More than 1000 particles of each specimen were measured on magnified electron micrographs.

By following every particle of the same region of a specimen after each heating, our experiments show that crystallite migration and coalescence plays a role in the sintering of the model catalyst. The mobility of the crystallites depends upon the treatment conditions. Different regions of at least four specimens were examined for each of the experimental conditions.

Effect of Chemical Atmospheres

Table 1 shows that little sintering occurs on the specimens heated in high vacuum, H_2, N_2, O_2, and wet N_2 at 500, 650, or 750°C. Significant crystallite sintering occurred when the specimens were heated in wet H_2. The size distributions of the Pt crystallites for the fresh specimen and for the same specimen heated in wet H_2 are shown in Fig. 1. The fresh specimen has a sharp size distribution around 5 nm (Fig. 1a). After heating in wet H_2, the number of crystallites decreased, and the size of the crystallites increased. The size distribution curve broadened dramatically, and the average size increased to 9, 11, and 16 nm, respectively (Figs. 1b to 1d). Furthermore, the size distributions have a Gaussian shape and develop tails toward the large crystallites with increasing heating temperature and time.

The electron micrographs of Figs. 2a and 2b represent nearly the same region of a specimen heated in wet H_2 at 650°C for 1 and 4 hr, respectively. In order to detect better the changes that occurred, Fig. 2a is overlapped (after proper rotation) with Fig. 2b in Fig. 3. It should be noted that some minor modifications in the morphology of the substrate, such as the broadening of grain boundaries, seem to occur. The relative positions of the grains remains, however, unchanged. In Fig. 3, the particles marked by solid lines represent the distribution after heating 1 hr, and those marked by broken lines represent the distribution after heating 4 hr. Solid lines mark also some grain boundaries to identify relative positions in both specimens. Upon close examination of the micrographs of Fig. 3 a large number of interesting events can be observed. For example, crystallites 1 to 4 of diameters of the order of 10 nm migrated about 5 to 12 nm in 3 hr of heating to form


2a
40 nm

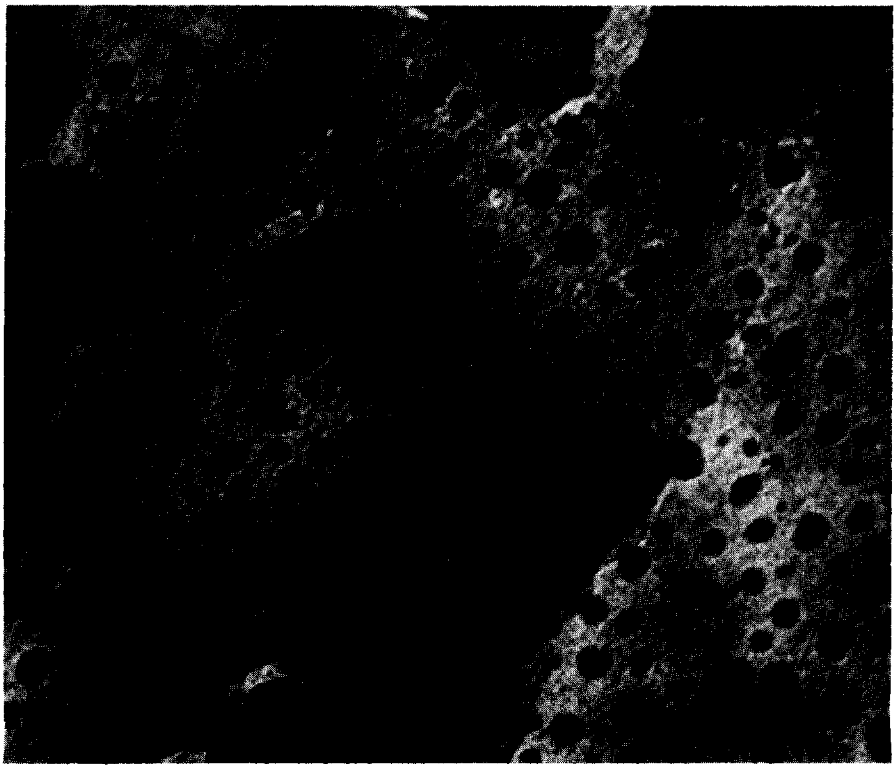


FIG. 3. Diagram showing the positions of the particles on the substrate from Fig. 2a, solid lines, and Fig. 2b, broken lines.

crystallite 5. Crystallite 5 has a position where no large crystallites were present previously. Crystallite 6 either migrated to join in sintering with crystallites 1 to 4 to form crystallite 5 or migrated to join in sintering with crystallites 7 to 9 to form crystallite 10. It is difficult to identify the previous locations of crystallites 11 and 12 of about 10 and 12 nm diameter. They have been formed either through the migration of small crystallites or have migrated large distances from other positions. In 3 hr crystallites 13 and 14 of about 15 and 13 nm diameter displaced distances of about 7 and 4 nm. Furthermore, the size of the newly formed crystallite 15 is about the sum of the diameters of crystallites 16 and 17, while the size of crystallite 10 is somewhat larger than the sum of the diameters of crystallites 7 to 9. It is apparent that large crystallites are composed of separated crystallites which have moved toward each other to sinter but without organizing into a single thick crystallite. The sintering behavior of specimens heated in atmospheres other than wet H_2 is similar, but crystallites larger than 5 nm in diameter are almost immobile. The growth of crystallites took place through migration of crystallites smaller than 5 nm in diameter. Since the number of such crystallites is small, the size increase of the crystallites is also small (see Table 1).

The sintering of Pt crystallites in O_2 or H_2 atmospheres is low. However, after a number of alternative heatings in O_2 or H_2, the crystallites redisperse during heating in O_2 and sinter during heating in H_2. These phenomena have been explained in terms of wetting (*20*). Only the results

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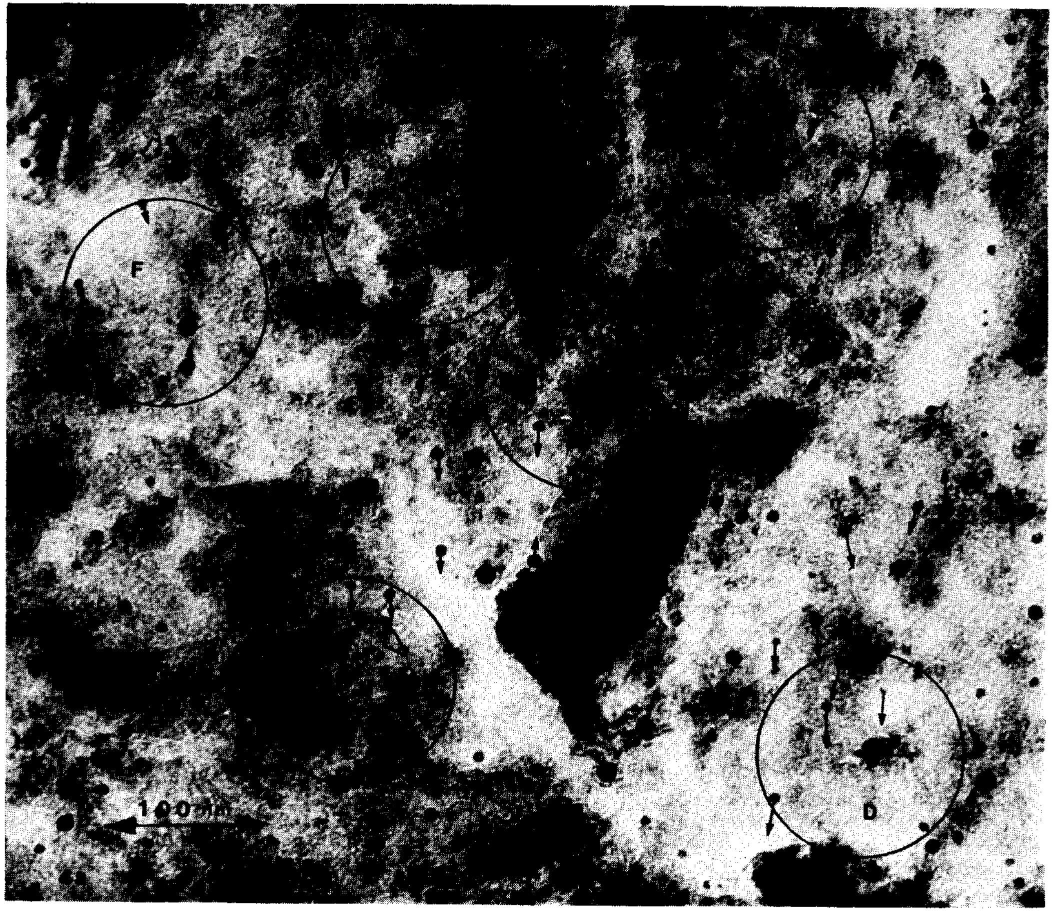
FIG. 2. Transmission electron micrographs of the model catalyst showing the effect of heating in wet H_2. To follow the changes of the same region the same specimen was heated at 650°C under 1 atm of wet H_2 for (a) 1 hr and (b) an additional time of 3 hr.


F
100 nm
D

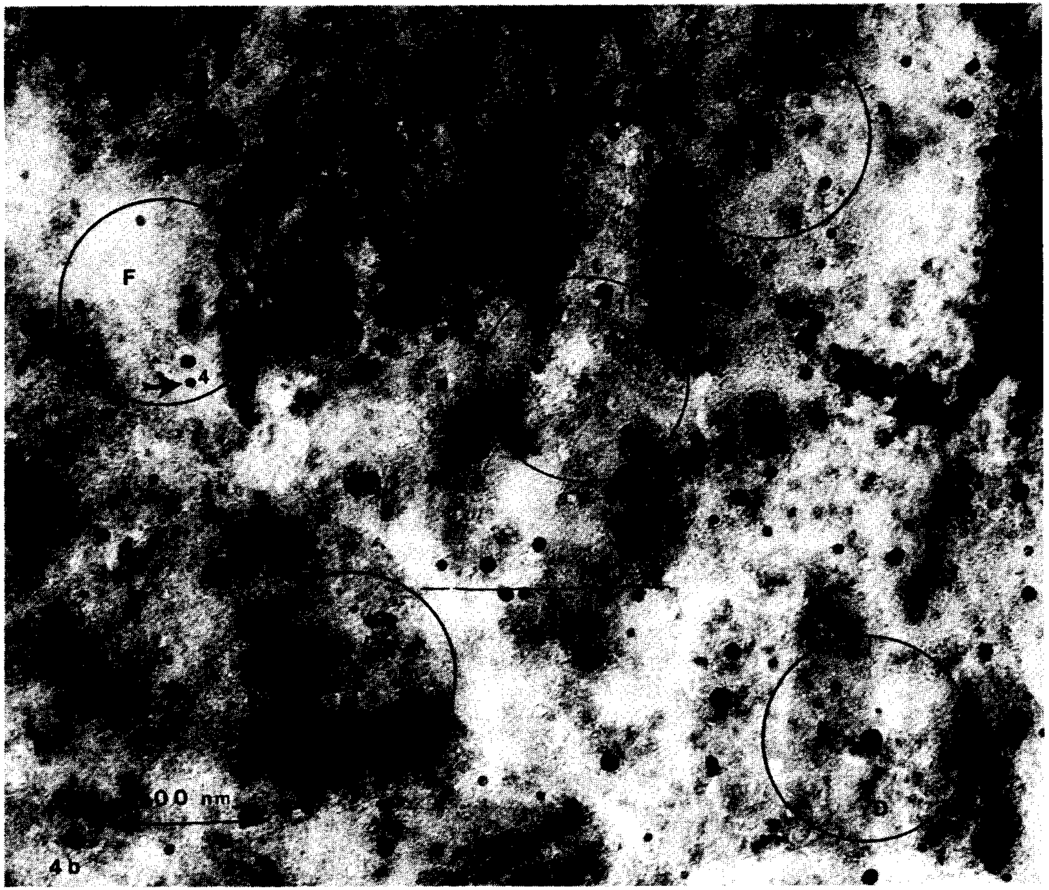
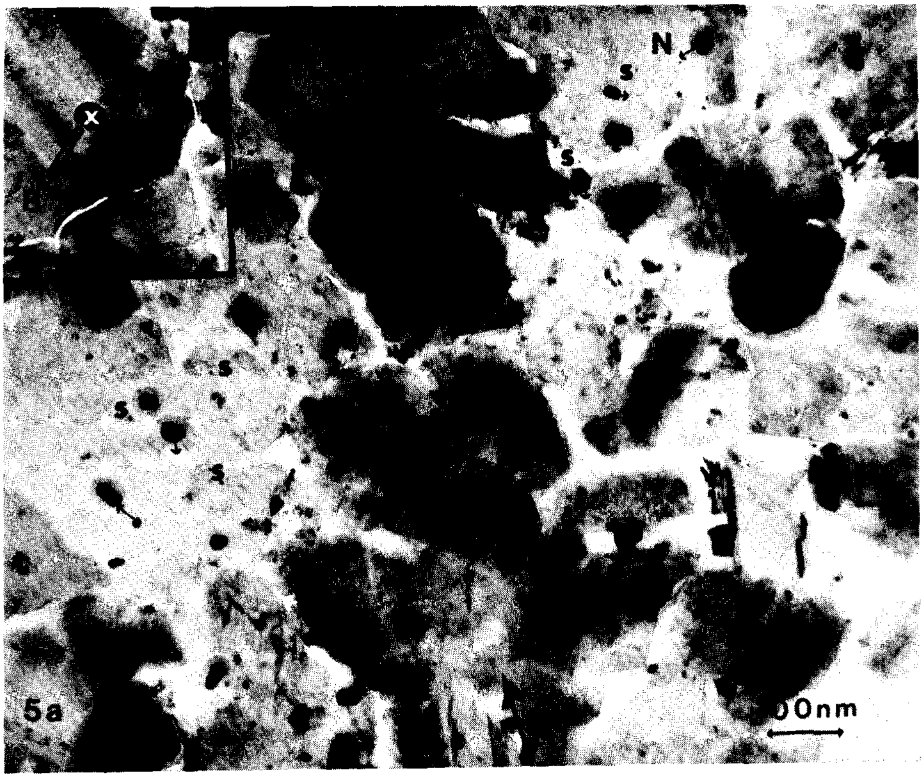


Fig. 4. Transmission electron micrographs of the model catalyst showing the effect of periodic heating in O_2 and H_2. (a) The specimen was heated at 750°C periodically in oxygen and hydrogen of 1 atm for a total of 72 hr. (b) The specimen of Fig. 4a was further heated in H_2 at 850°C and 1 atm for 1 hr. The electron micrographs show that crystallites as large as 10 nm in size migrate on the surface. In Fig. 4a the arrows indicate the possible direction of crystallite migration.


x
N
s
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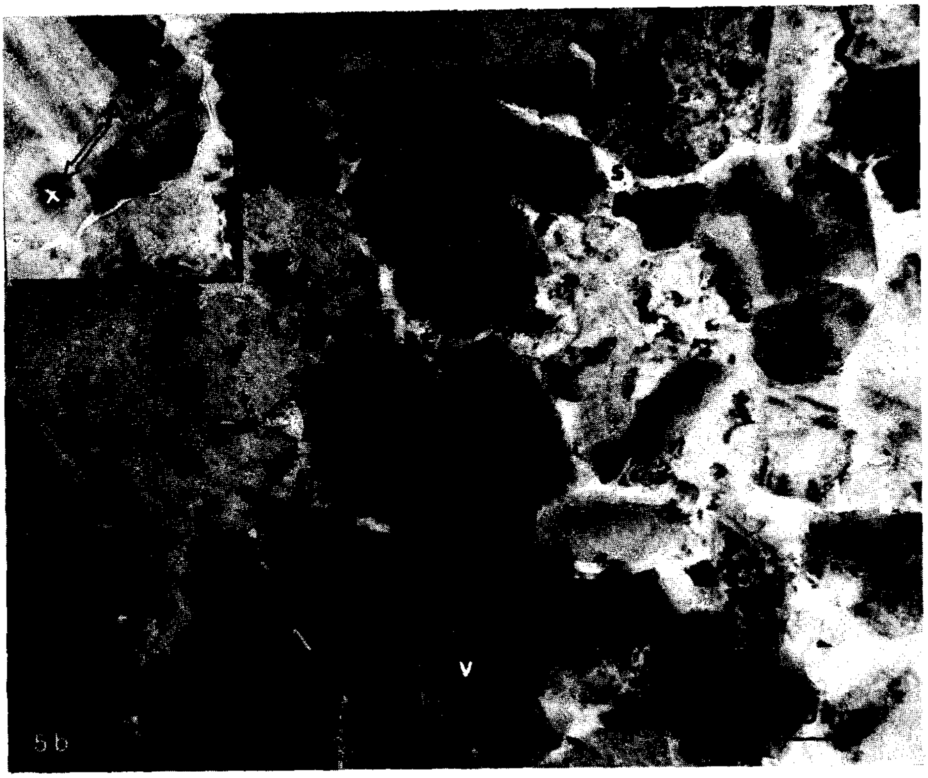
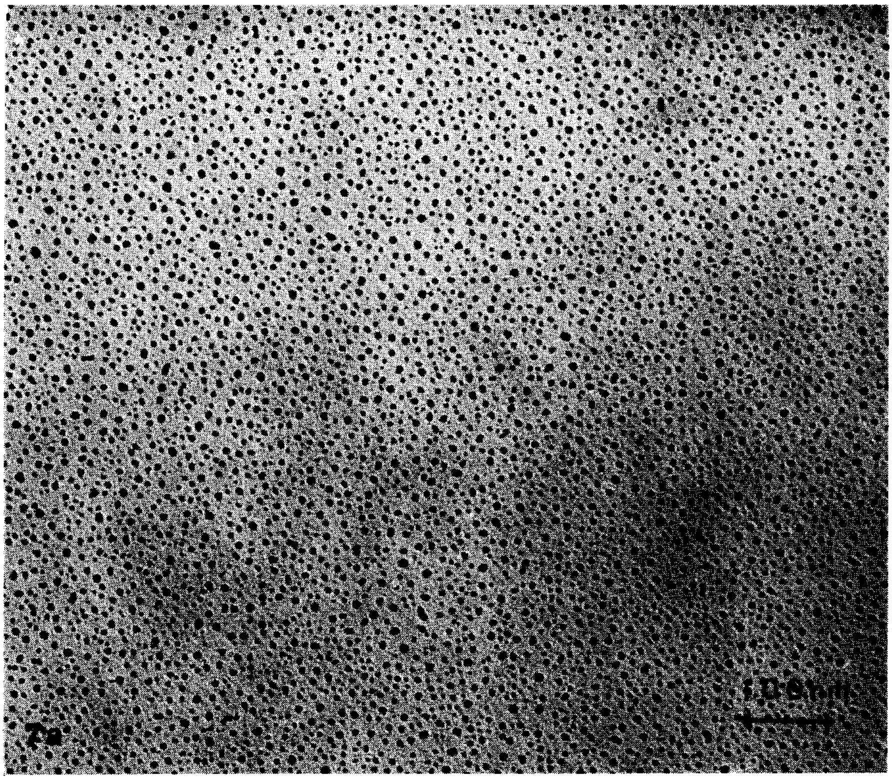

x
s
v
5b

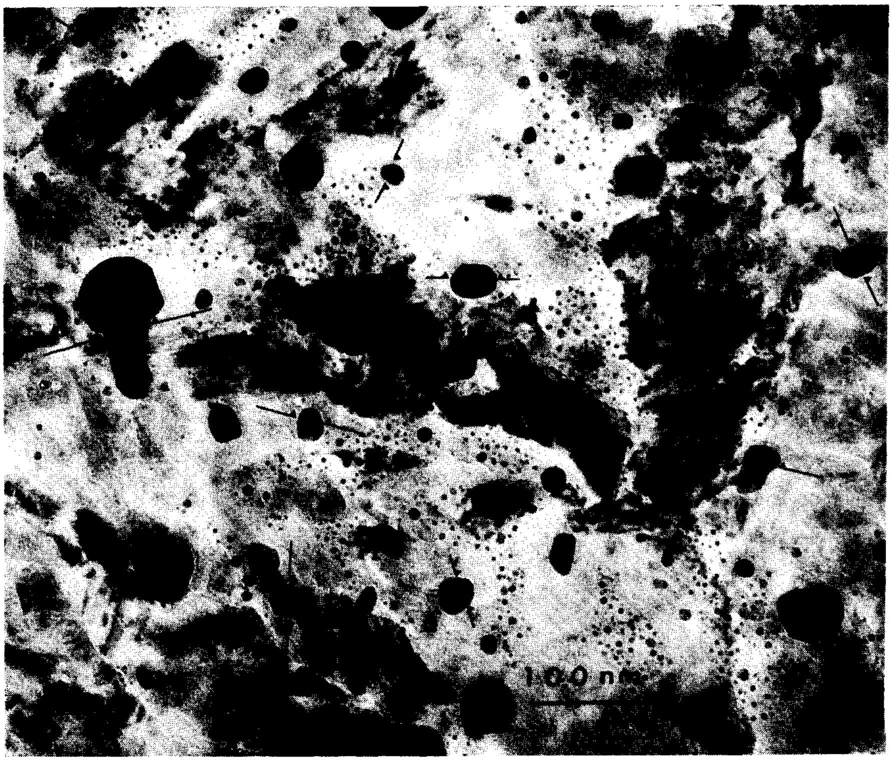
FIG. 6. Transmission electron micrograph showing the effect of burning off of the carbon from a carbon-coated model catalyst. Pt crystallites left tracks and impressions on the alumina surface after the carbon-coated model catalyst was heated for 1 hr at 500°C in O_2 of 10^{-2} Torr.

related to sintering are, however, examined here. The electron micrograph of Fig. 4a shows the specimen which has been heated periodically in oxygen and hydrogen atmospheres for a total of up to 72 hr. Each cycle contains a 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. The final treatment in this succession consisted of heating, at 1 atm for 1 hr in O_2 and 750°C followed by 1 hr in H_2 at 750°C.

The average crystallite size has changed during this periodic treatment from about 3 to about 10 nm. The specimen of Fig. 4a has been further heated in H_2 at 850°C and 1 atm for 1 hr (Fig. 4b). It is clear from the electron micrographs that crystallites as large as 10 nm in size migrate on the surface. The regions of interest are encircled by solid lines for easier identification of particles. Arrows indicate the possible direction of crystallite migration. In region A, crystallite 1 of about 10 nm diameter migrated upward a distance of about 23 nm in 1 hr of heating at 850°C. Crystallite 2 of about 8 nm migrated downward a distance of about 13 nm in 1 hr. In region B, crystallite 3 of about 7 nm diameter migrated about 18 nm also in 1 hr. In regions

FIG. 5. Transmission electron micrographs of a model catalyst after sintering in air at 850°C for 6 hr. (a) The sample was further coked by the decomposition of acetylene at 750°C and 2 Torr for 0.5 hr. Carbon deposits build up around the crystallites. (b) The specimen of Fig. 5a is regenerated by heating for 1 hr at 850°C in 20% O_2 in N_2 of 1 atm. During regeneration, crystallite migration occurs.


100nm
7a


100 nm

C, E, and near F crystallites indicated by large arrows show sintering of two colliding crystallites. In region F of Fig. 4b, crystallite 4 appeared without a clear evidence of its previous location. It should be noted that further treatment of this specimen in H_2 at the same temperature did not cause further significant crystallite migration.

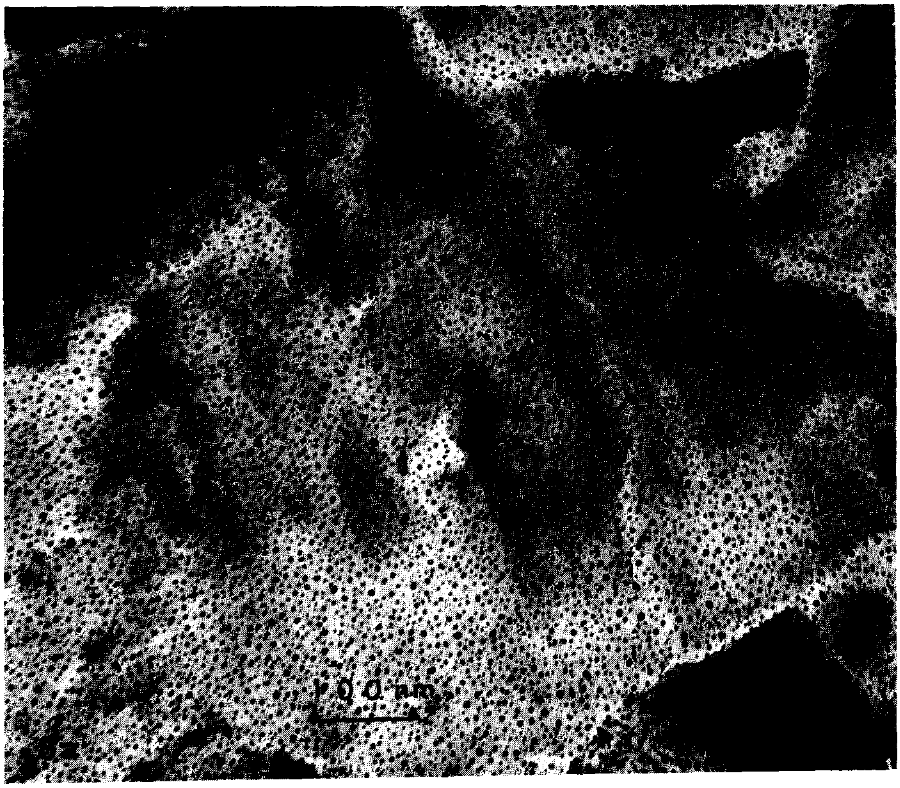
Crystallite migration, in wet H_2 and during severe reduction after cyclic treatment in O_2 and H_2 atmospheres, is probably enhanced by the water produced by the reduction of oxidized Pt. Oxygen oxidizes the metal to platinum oxide, and hydrogen reduces the oxide generating H_2O between the Pt particle and the substrate. This weakens the interaction between Pt particles and the substrate and hence enhances crystallite migration. The weakening is intensified by the repetition of the cycles. In the wet H_2 atmosphere, crystallite migration was probably caused by oxidation by water followed by reduction by H_2. This also weakens the bonds between crystallites and substrates. It should be noted that the wet N_2 atmosphere did not have the same effect as the wet H_2 atmosphere on sintering (see Table 1). This seems to indicate that water oxidizes Pt as oxygen does. Only the water produced during reduction of Pt oxides which weakens the interaction between Pt particle and substrate enhances crystallite migration. After prolonged treatment by hydrogen following cyclic treatment by O_2 and H_2 no further sintering occurs. This is probably because the Pt oxide is completely reduced, and no more water is formed.

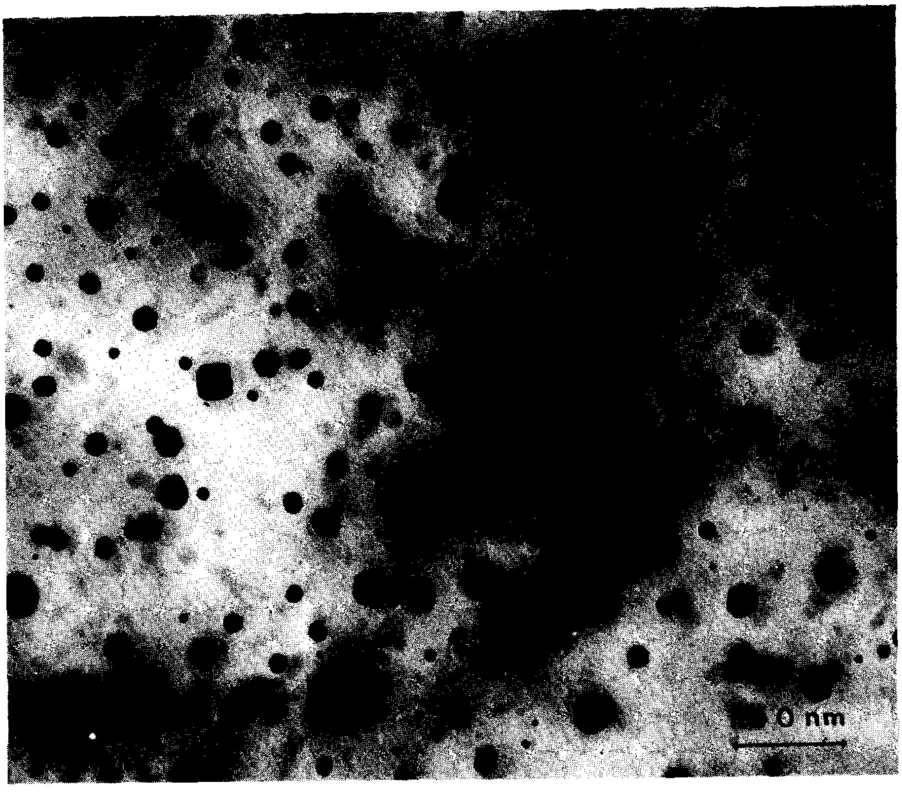
Experiments on model catalysts have been previously carried out to study the effect of oxygen on sintering (*4, 21*). Wynblatt and Gjostein (*4, 21*) observed that heating the specimen in laboratory air appreciably increased sintering. However, heating in 2% O_2 in N_2 at 1 atm pressure had no appreciable effect. A group of experiments have been carried out by us by heating the model catalyst used here in laboratory air. The conclusions are similar to those of references (*4*) and (*21*). The moisture content of the laboratory air probably explains the difference in behavior.

Effect of Regeneration of Coked Catalyst by Oxidation

Significant crystallite migration occurs during regeneration of the catalyst by burning off the carbon deposited on the crystallite surface (*22, 23*). The electron micrographs of Fig. 5 represent the same region of two specimens both before and after regeneration. The specimen of Fig. 5a has been prepared by heating the model catalyst in air at 850°C for 6 hr followed by coking the sample by the decomposition of acetylene at 750°C and 2 Torr for 0.5 hr. As shown in Fig. 5a, during coking, carbon deposits build up around the crystallites mostly along the peripheries and perhaps on their surface. Regeneration was carried out with 20% O_2 in N_2 at 850°C and 1 atm pressure for 1 hr. During regeneration crystallite migration occurs (see Fig. 5). Crystallite x in Fig. 5 of about 30 nm diameter migrated from position A to position B, about 130 nm, within 1 hr. It is likely that crystallites T and U in Fig. 5a of about 25 nm diameters migrated about 90 and 110 nm to sinter into one single crystallite V of about 37 nm diameter. Crystallite N in Fig. 5 also underwent crystallite migration and sintering. The large distance covered by the migration of large crystallites is obviously caused by the gases resulting from the catalytic oxidation of the carbon accumulated along the

Fig. 7. Transmission electron micrographs of the model catalyst showing the effect of substrate crystallization. The amorphous alumina crystallizes to γ-Al_2O_3. (a) Initial state; (b) after heating for 24 hr at 550°C and 10^{-6} Torr.


100 nm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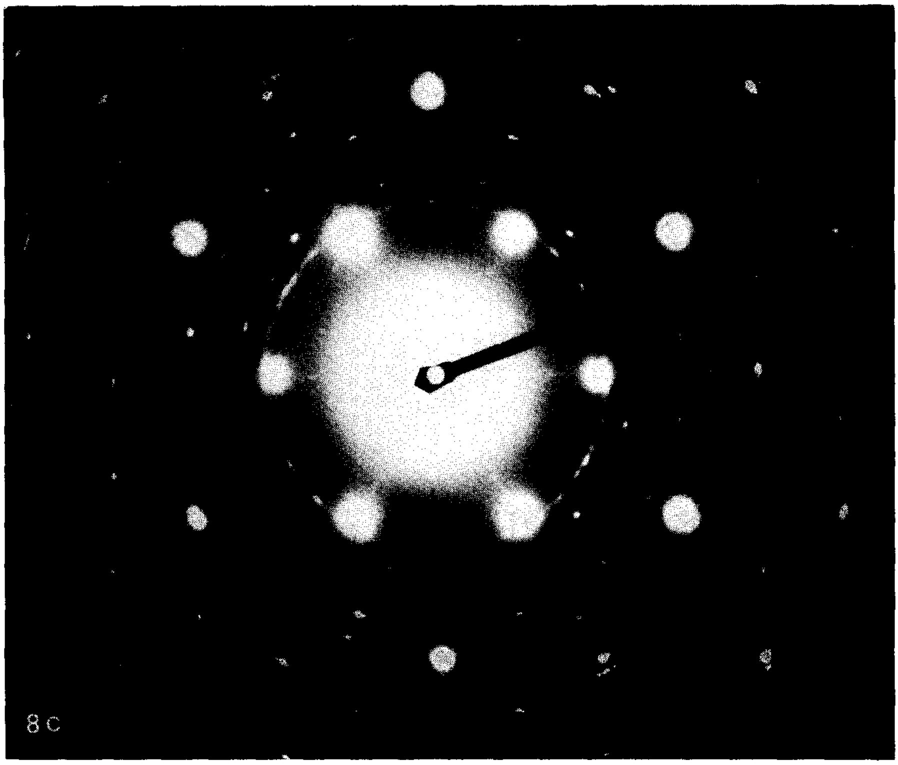


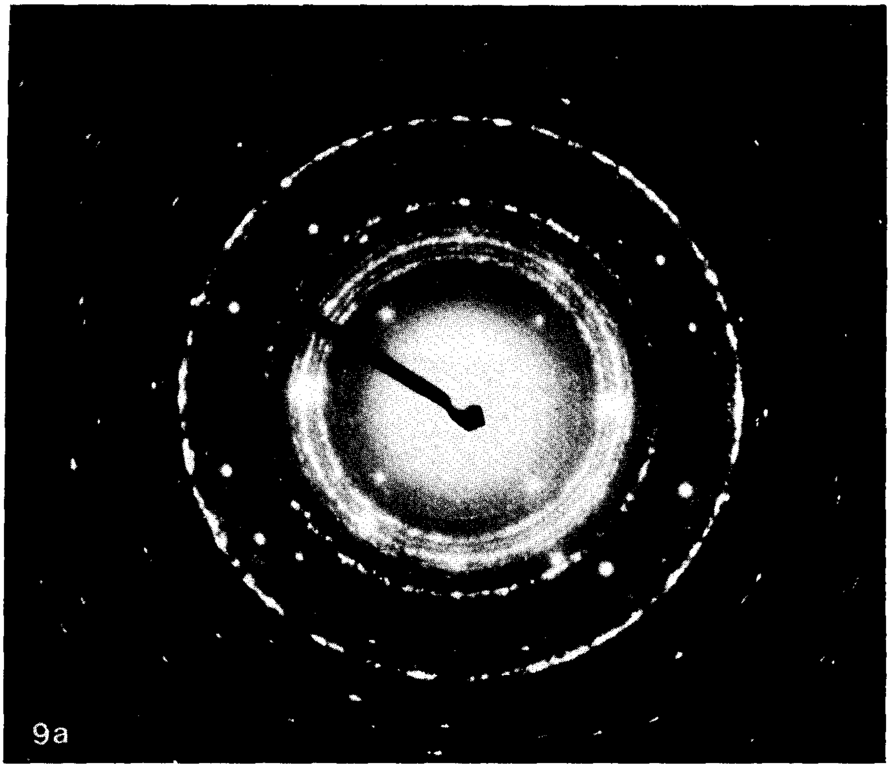
FIG. 8. Transmission electron micrograph of the model catalyst showing the effect of phase transformation of alumina. (a) The initial state; (b) after heating at 850°C in a H_2 pressure of 10^{-4} Torr for 6 hr γ-Al_2O_3 transforms to α-Al_2O_3 and faceted crystallites are overlapping each other. (c) Electron diffraction pattern corresponding to the specimen of Fig. 8b. The bright spots correspond to α-Al_2O_3, and the rings correspond to Pt.

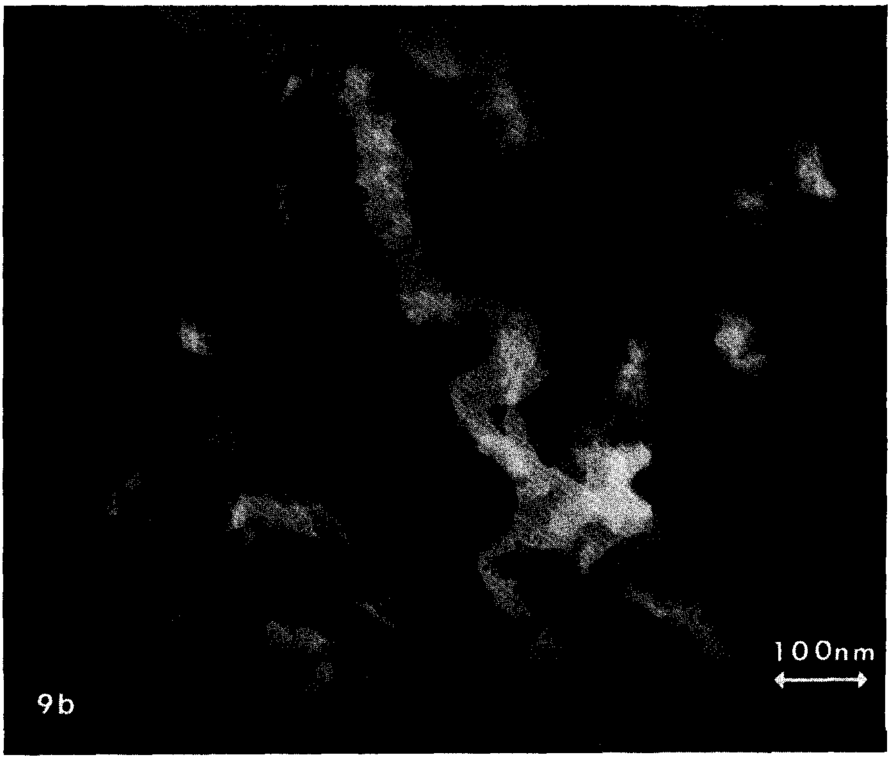
peripheries of the crystallites and on the metal surface. Very small crystallites identified by "S" in both figures are immobile during the regeneration process. Probably the amount of gases produced by the oxidation of carbon from the small crystallites is too small to lift the small crystallites trapped in the pores. If a carbon-coated Pt model catalyst is heated in O_2 at 10^{-2} Torr and 500°C for 1 hr, Pt crystallites are found to leave tracks on the alumina surface (see Fig. 6). A similar observation was made previously when studying sintering of Pt on carbon substrates (*15*). The gases evolved during the catalytic oxidation of carbon probably lift the crystallites and thus cause migration. The tracks record the route of the travelling crystallites.

Effect of Phase Transformation of the Substrate

Fast sintering occurs on a substrate which undergoes phase transformation. A film of Pt deposited on amorphous alumina was heated in H_2 at 400°C and 1 atm for 6 hr. As shown by electron diffraction the substrate preserved its amorphous character during the treatment. After heating in a vacuum of 10^{-6} Torr at 550°C for 24 hr, the substrate crystallized to γ-Al_2O_3. In association with this phase transformation, Pt crystallites sinter severely (Fig. 7).

Another experiment was carried out to transform γ-Al_2O_3 to α-Al_2O_3 and to observe the behavior of Pt. Fresh specimens were heated at 850°C in a H_2 pressure of 10^{-4} Torr for 6 hr. γ-Al_2O_3 was transformed to


9a


100nm
9b

α-Al_2O_3, and severe sintering occurred (see Fig. 8). The arrayed spots in the electron diffraction pattern of Fig. 8c are characteristic of α-Al_2O_3 while the rings are characteristic of Pt. The large crystallites in Fig. 8b facet and overlap each other. When heating in air of 1 atm, the transformation of γ-Al_2O_3 to α-Al_2O_3 generally occurs at temperatures higher than 1100°C (*24*). In the present experiments, the presence of Pt and/or H_2 has lowered the temperature at which this phase transformation occurs.

Effect of Reaction between Pt and Substrate

By heating fresh specimens in a vacuum of 10^{-6} Torr and 850°C for 6 hr, not only did the substrate undergo phase transformation to α-Al_2O_3 but the Pt crystallites also reacted with the substrate. The complex electron diffraction pattern shown in Fig. 9a is identified to correspond to a mixed pattern of Pt_8Al_{21}, Pt, γ-Al_2O_3, and α-Al_2O_3. Figure 9b shows the resulting microstructure. The shallow tracks indicate the portion of alumina removed by Pt for alloying to take place. High reactivity probably enhances the mobility of the Pt particles because the substrate becomes weaker. The formation of similar intermetallic compounds was identified by a number of authors in a variety of conditions (*25–28*).

FINAL REMARKS

For the model catalyst system used here crystallite migration and coalescence are responsible at least in part for sintering. The mobility of the Pt crystallites depends upon the treatment conditions. Migration of crystallites is enhanced by increase in temperature, periodic oxidation and reduction, reaction of Pt with substrate, and burning off of coke from Pt surface. Macroscopic movements of the substrate during phase transformation of alumina also enhance crystallite sintering. These mechanisms may also play a role in the sintering of commercial catalysts. The observation that oxygen does not significantly promote sintering is valid, however, for the model catalyst only. Experiments to be reported elsewhere (*29*) show that the industrial catalysts sinter rapidly while heated in oxygen. This difference in behavior arises from differences in catalyst preparation. In the present case the metal was deposited by vacuum vaporization. It will be shown (*29*) that a platinum–chloride complex exists in the commercial catalyst which probably plays a role in sintering.

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FIG. 9. (a) Electron diffraction pattern corresponding to the specimen of Fig. 9b. (b) Transmission electron micrograph of the model catalyst showing the effect of reaction between Pt and substrate after heating at 850°C and 10^{-6} Torr pressure for 6 hr. Pt migrates, reacting with alumina and leaving tracks on the alumina surface. The large black particles are Pt_8Al_{21} alloy, and the substrate is a mixture of γ- and α-Al_2O_3. The initial state is similar to that of Fig. 8a.

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