

The Sintering of Platinum Particles in an Alumina-Supported Catalyst: Further Transmission Electron Microscopy Studies

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Transmission electron microscopy was used to investigate platinum particle sintering in specimens of a Pt/Al₂O₃ catalyst heat-treated under oxidising conditions. The specimens were prepared by a novel technique based on the sol-gel process. It was found that heating in air at 700°C produced very rapid sintering, the mean particle diameter increasing from 50 to 300 Å after 8 h. The form of the particle size distributions, and the types of particle structure observed in sintered catalysts, suggested that the mechanism involved a combination of migration and coalescence of whole particles and Ostwald ripening. A significant proportion of the particles exhibited abnormally rapid growth, and these particles were often twinned. In some cases the accelerated growth could be attributed to the presence of reentrant surface features at the twin boundaries: such features would act as preferential nucleation sites in the Ostwald ripening mechanism. It is possible that some of the twin boundaries may originate from particle coalescence. © 1986 Academic Press, Inc.

INTRODUCTION

Much care is taken in the preparation of supported metal catalysts to ensure that the mean particle size is as small as possible, so that the ratio of surface metal atoms to bulk metal atoms is maximised. While this produces an initially high activity, the large surface energy per unit volume of metal can act as a powerful driving force for the growth, or sintering, of the particles, with consequent deactivation of the catalyst. This is a serious problem in the operation of supported metal catalysts, and one which has received much attention in recent years (1, 2). Many studies have been carried out with the aim of determining as accurately as possible the variation in mean particle size or particle size distribution as a function of heat treatment, and comparing these data with the predictions of theoretical models. In this way it is hoped to establish which of the two possible mechanisms for sintering, namely migration and coalescence of whole particles or Ostwald ripening, predominates under particular conditions. Of the various methods which have been employed in these studies, transmission elec-

tron microscopy (TEM) is undoubtedly the most useful since this enables a direct determination of the particle size distribution. In addition, information on the structure of individual particles in heat-treated catalysts can be obtained, which may provide further insights into the sintering mechanism.

The present work comprises an extension of previous TEM studies into the sintering behaviour of an alumina-supported platinum catalyst under oxidising conditions (3). It is hoped that the results may have some relevance to the deactivation of operational vehicle exhaust catalysts. A novel specimen preparation technique has been employed, which enables thin films of catalyst to be prepared directly on microscope grids, thus avoiding the necessity to thin the bulk material mechanically. The method is based on a process for applying catalytic coatings onto metal sheets (4), and involves the use of an aqueous alumina sol. In the earlier study (3) it was shown that heating the catalyst specimens at 600°C in 1 atm of air produced rapid platinum particle sintering, with the mean particle diameter increasing from 50 to 109 Å in a period of 24 h. A consideration of the particle size distri-

butions led to the conclusion that the predominant mechanism during the early stages of sintering was probably migration and coalescence of whole particles. After about 2 h the kinetics of sintering appeared to undergo a change, interpreted as indicating a change in the predominant mechanism from migration and coalescence to Ostwald ripening (interparticle transport). In specimens heated for 8 h or longer, some of the particles were observed to be growing abnormally rapidly compared to the majority of the population. These large particles possessed a variety of structures, but some of them were clearly plate-like or rod-like in overall shape. Similar anisotropically growing particles had been observed previously by Wynblatt and co-workers in studies of model platinum/alumina catalysts (5, 6). It seems certain that crystallites with these forms grow by Ostwald ripening, since particle coalescence would be expected to produce shapes with a lower surface area-to-volume ratio. Microdiffraction patterns of some of the plate-like particles could be interpreted as [111] with extra spots of the type $1/3 \{422\}$, indicating that a twin boundary or boundaries were present perpendicular to the beam direction. Cosandey *et al.* (7) have recently reported similar patterns from plate-like platinum particles in both model and real catalysts, and have also directly observed the presence of two parallel twin boundaries in such particles by tilting them to an edge-on position. These authors discuss the ways in which the twin boundaries could produce the observed rapid plate-like growth, but do not come to any definite conclusion. Overall, there remain a number of important questions to be answered concerning "abnormal growth." For example, it is not clear whether twins play a rôle in the growth of large particles which are not plate-like in shape. Moreover, the mechanism of twin formation is not known.

The experiments reported here were carried out under conditions which favoured "abnormal growth," i.e., a temperature of

700°C in 1 atm of air. In interpreting the results, a major aim will be to achieve a fuller understanding of the factors which contribute to this important phenomenon.

EXPERIMENTAL

The specimen preparation technique has been described in detail previously (3, 8). Briefly the procedure involved mixing a solution of tetrammine platinum(II) dichloride with an aqueous alumina sol (pH 4), dipping stainless-steel TEM grids into this mixture to produce a thin liquid film suspended across the squares, and then drying, firing, and reducing this to give thin sheets of catalyst extending out from the grid bars. The proportions of the two starting materials were such that the platinum loading in final catalyst was 6.3% by weight. The addition of a little wetting agent to reduce the surface tension of the sol was found to be helpful in forming thin catalyst films. It was sometimes difficult to avoid picking up too thick a film of liquid on the grid; this could be rectified by dabbing the grid onto a filter paper.

The microscope employed was a JEOL 200-CX instrument, operated at 200 kV. Figure 1 shows a typical freshly prepared specimen at low magnification. At higher magnification there was generally little difficulty in imaging the supported platinum particles. Several authors have discussed the problems that can arise in attempting to distinguish between contrast from supported particles and contrast from the sup-

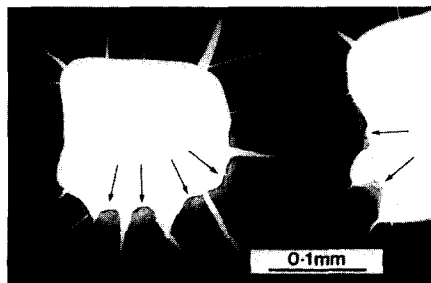


FIG. 1. Low-magnification micrograph of freshly prepared specimen. Thin areas are shown by arrows.

port (e.g., (9, 10)), but these problems were not serious in this study since the mean particle sizes were relatively large in most of the specimens examined.

Sintering was investigated by heat-treating specimens in laboratory air at 700°C for 10 min, $\frac{1}{2}$ h, 1 h, 2 h, 4 h, and 8 h. Particle size distributions were determined by measuring the diameters of 1000 particles in several different specimens which had undergone each of these treatments. For periods longer than 8 h at 700°C the very broad range of particle sizes made a reliable determination of the size distribution difficult. A large number of high-magnification bright field images of individual particles in specimens sintered for 2 h at 700°C were recorded, in order to investigate the types of structure present. Some selected area diffraction patterns of very large particles in specimens sintered for 8 h were also recorded. In addition a few specimens heated for 24 h at 700°C were examined, with the specific purpose of investigating the detailed structure of very large plate-like particles.

X-Ray microanalysis was carried out on fresh and sintered specimens, and revealed traces of Cl and S on the support. There is no reason to suppose that the presence of such contamination at very low levels would affect the sintering behaviour significantly.

A number of experiments involving the examination of the same area of a specimen before and after heat treatment were attempted, but these were unsuccessful. It was found that specimens which had been examined in the microscope and subsequently heat-treated exhibited a considerably inhibited degree of sintering. This was probably a consequence of the deposition of a contaminating carbonaceous layer on the platinum surface while in the microscope. It is interesting to note in this connection that Baird *et al.* (11) have suggested that surface carbon can inhibit the sintering of platinum black catalysts. These observations indicate that experiments aimed at ob-

serving the same area of a catalyst before and after sintering require the use of an ultrahigh vacuum microscope, so that carbonaceous contamination is avoided.

RESULTS AND DISCUSSION

Figure 2 shows a typical freshly prepared specimen, and Figs. 3 and 4 show specimens heated for 2 and 8 h at 700°C in air, illustrating the very rapid platinum particle sintering which occurs under these conditions. Figure 5 shows a lower magnification micrograph of a specimen heated for 8 h at 700°C. In this section it is hoped to elucidate the mechanism of sintering by analysing the particle size distributions and the kinetics of the process, and by considering the structures of particles in sintered catalysts. A brief discussion of the origin of twinned particles will also be given.

Analysis of Sintering Data

The particle size distribution for fresh specimens is given in Fig. 6, and those for specimens heated for 10 min, $\frac{1}{2}$ h, 1 h, 2 h, 4 h, and 8 h in air at 700°C are given in Figs. 7a–f. These histograms are similar in their overall form to those for sintering at 600°C (3). Again we find well-defined lower limits: after 1 h there are no particles smaller than 40 Å in diameter, and after 8 h none smaller than 80 Å. As in the earlier study, we assume that migration and coalescence has occurred for particles smaller than these limits, since the complete disappearance of small particles would seem to be inconsistent with Ostwald ripening. The other obvious feature which the distributions have in common with those for 600°C is the long tail to the high-diameter side, arising from the presence of fast-growing particles. The commencement of abnormal growth occurs much earlier at 700°C than at the lower temperature; after only 30 min the distribution contains particles as large as 400 Å (Fig. 7b). After 8 h the tail extends to 2000 Å (Fig. 7f), and it is noticeable that the main part of the peak, centered on 170 Å, is wider and less well-defined here than in previous

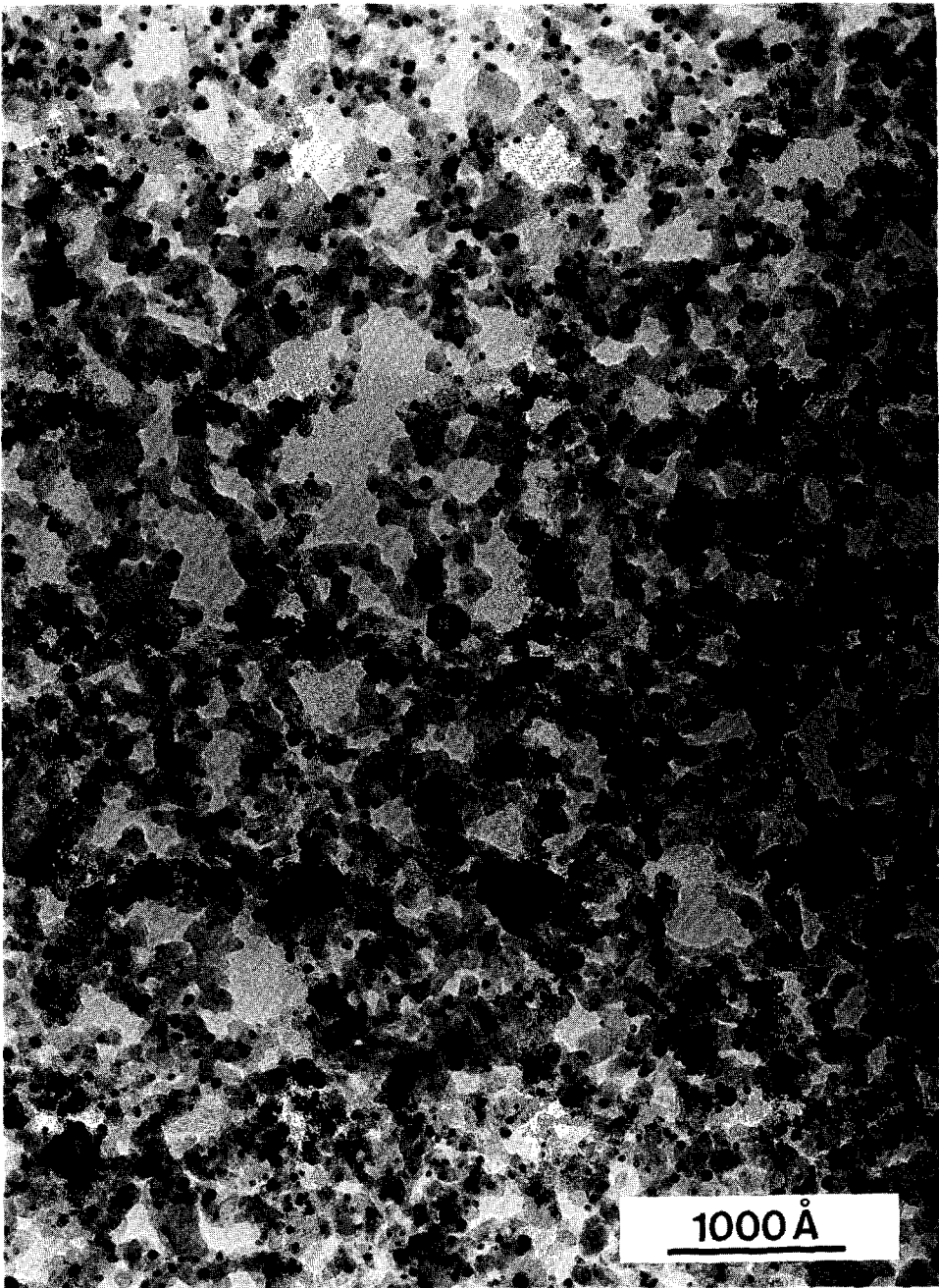


FIG. 2. Typical micrograph of freshly reduced specimen.

distributions. It seems likely that this trend would continue for longer heat treatments, resulting in an extremely broad range of particle sizes with little or no peak at the low-diameter end. As mentioned in the Introduction, the shapes of many of the ab-

normally large particles are indicative of an Ostwald ripening growth mechanism. Overall, therefore, the particle size distributions indicate that both migration and coalescence and Ostwald ripening occur, with the latter becoming increasingly predominant for

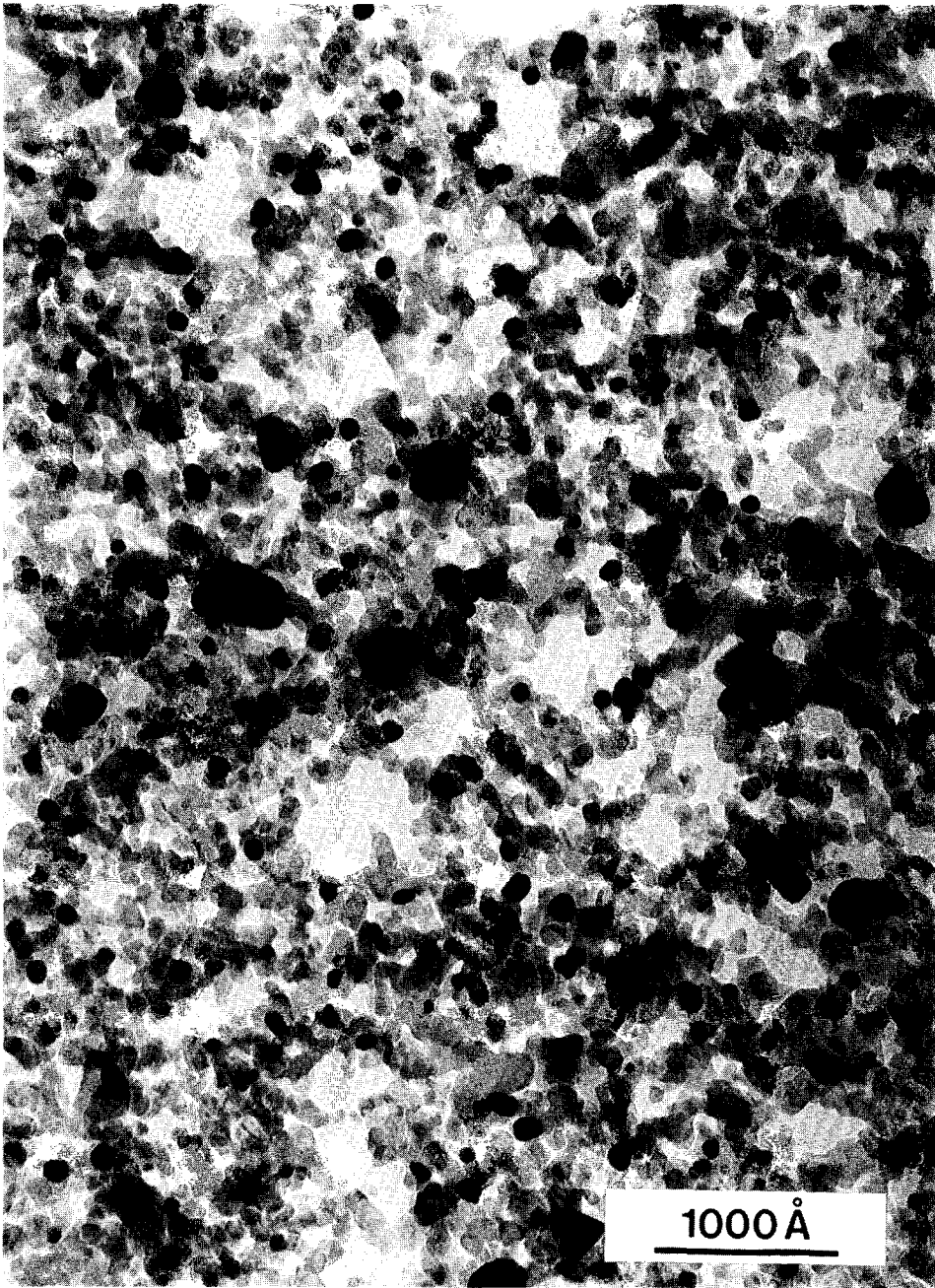


FIG. 3. Typical micrograph of specimen heated at 700°C in air for 2 h.

longer sintering times. Under the strongly oxidising conditions employed here the probable mode of Ostwald ripening would be transport of PtO_2 through the vapour phase (12). Crystalline PtO_2 was not detected in any of the sintered specimens.

The variation in mean diameter with time for heat treatments at 700°C in air is given in Table 1. In order to determine the kinetics of sintering it is usual to fit the data to a simple equation of the form (13, 14)

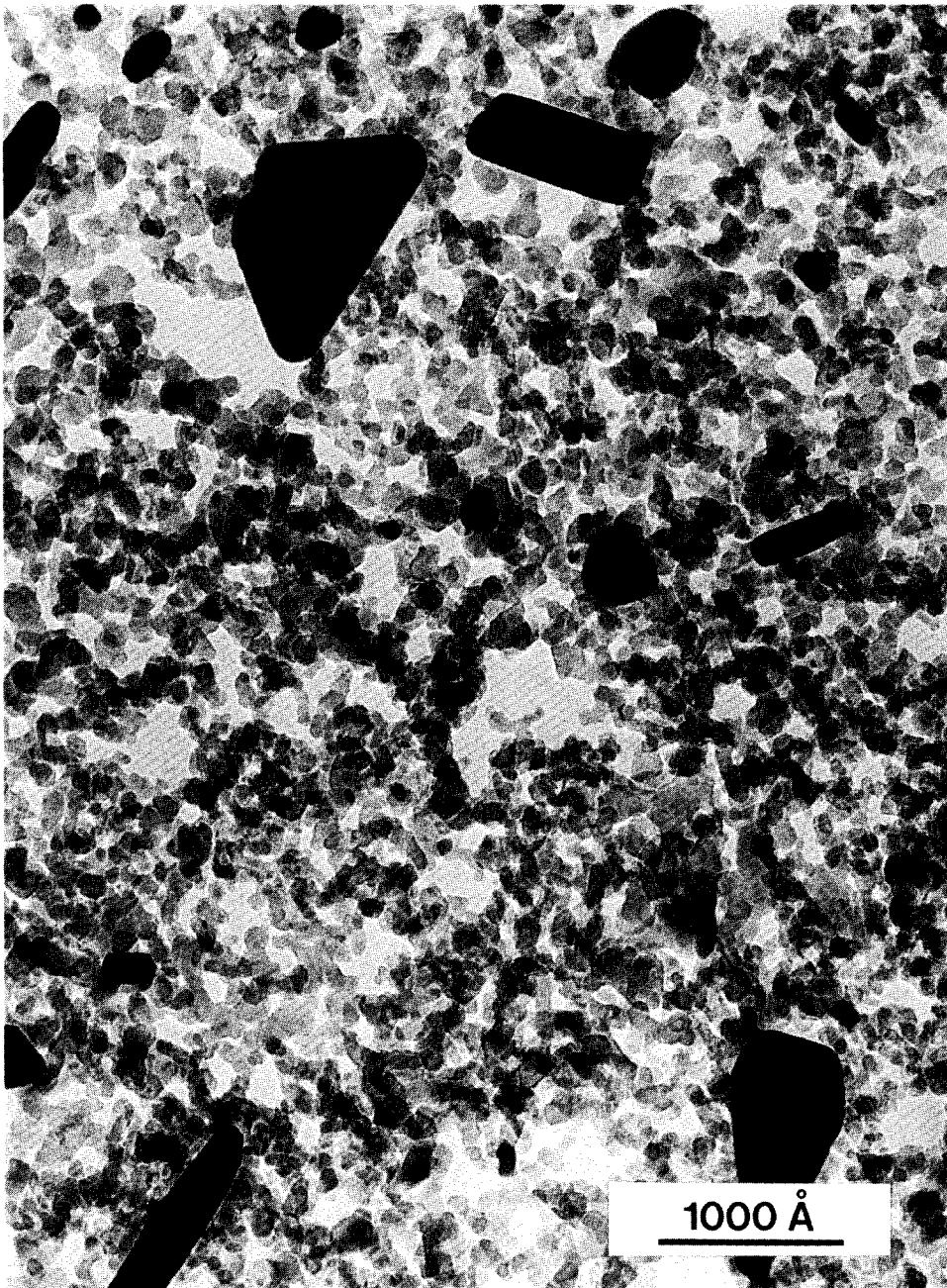


FIG. 4. Typical micrograph of specimen heated at 700°C in air for 8 h.

$$\bar{d}^n - \bar{d}_0^n = Kt,$$

where \bar{d} is the mean diameter after time t , \bar{d}_0 is the initial mean diameter, n is an integer, and K is a temperature-dependent constant. (Some authors employ an equivalent

expression in terms of total surface area S , which is similar in form to a reaction rate law. In such an expression the "order" of sintering is $(n + 1)$.) To fit our results to the kinetic law we first plot $\log(\bar{d}/\bar{d}_0)$ vs $\log t$. The gradient of this line yields an approxi-

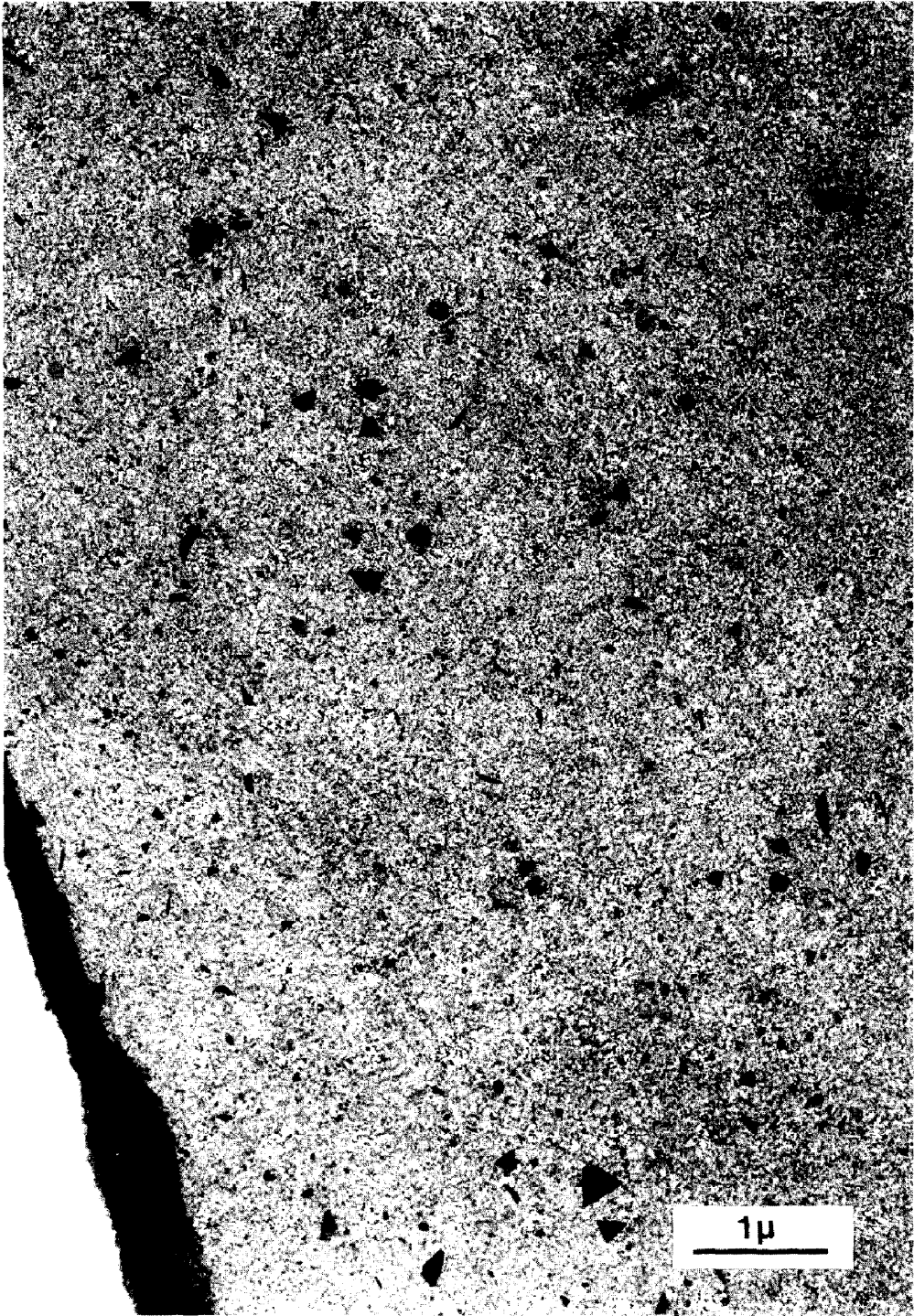


FIG. 5. Lower magnification micrograph of specimen heated at 700°C for 8 h.

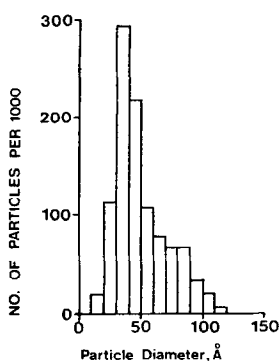


FIG. 6. Platinum particle size distribution for freshly prepared specimens.

mate value for the exponent n , and substitutions into the growth equation yield values of K which fit the data. The log/log plot is shown in Fig. 8 and appears to indicate a decrease in n from 4 to 1 after 4 h. The corresponding values of K are approximately $1.5 \times 10^8 \text{ Å}^4/\text{h}$. and $30 \text{ Å}^4/\text{h}$. A direct comparison of these kinetic parameters with the theoretical predictions would probably not be helpful since it appears that two distinct sintering mechanisms operate simultaneously under the conditions employed here. Moreover, it should be appreciated that in addition to the noninhibited Ostwald ripening exhibited by fast growing particles, smaller particles might experience growth by nucleation-inhibited Ostwald ripening (12). However, despite the complexity of the sintering behaviour the log/log plot is of value in revealing that the kinetics for the period 4–8 h are significantly different from those for the period 0–4 h. This change reflects the increasing predominance of fast growing particles which can be seen in the size distribution after a heat treatment of 8 h (Fig. 7f).

Platinum Particle Structure

Before discussing particle structure it should be emphasised that a high proportion of particles in both fresh and sintered catalysts could not be assigned to any specific structural classification, either because they were irregular or because their orien-

tation made identification difficult. In particular, it was often impossible to determine whether or not a particle contained twin boundaries, since these could only be seen under favourable conditions. Despite these difficulties it was clear that significant changes in the distribution of particle structures occurred during sintering. These will now be outlined, and micrographs of individual particles in sintered catalysts discussed in detail.

Freshly prepared catalysts. In fresh catalysts the majority of particles were single crystals, and the type of contrast obtained suggested that they were three-dimensional rather than raft-like in form. The particles were often slightly faceted, and sometimes appeared to be approximately octahedral in shape. Only a small proportion (1–2%) clearly contained single twin boundaries, and multiply twinned particles were rarely observed. However, this may have been partly because internal features are especially difficult to image in very small particles.

Heat-treated in air at 700°C for 2 h. After this heat treatment the proportion of twinned particles had definitely increased, even taking into account the greater ease with which twin boundaries could be imaged in larger particles. Nevertheless, most of the particles still appeared to be single crystals, particularly those smaller than $\sim 150 \text{ Å}$ in diameter. As in the fresh catalyst, many of

TABLE I

Mean Platinum Particle Sizes for Catalysts Heated in Air at 700°C, with 95% Confidence Limits	
Sintering time (h)	Mean diameter, \bar{d} (Å)
0	50 ± 1
0.167	75 ± 2
0.5	92 ± 3
1	113 ± 5
2	140 ± 8
4	152 ± 10
8	300 ± 25

these single crystals exhibited a slight degree of faceting and in some cases could be described as rounded octahedra; an example is shown in Fig. 9a. The total number of particles which were clearly twinned was ~20%. Of these, the majority were relatively small single twins, an example of which is shown in Fig. 9b (direct evidence that the boundaries observed in sintered catalyst particles are twins rather than randomly oriented grain boundaries is provided by lattice imaging (8)). Sometimes much larger singly twinned particles were seen, and such particles often appeared to have the approximate shape of triangular bipyramids, as in Fig. 9c. Occasionally it was observed that one or both of the twin-related segments in a singly twinned particle contained a thin layer of crystal which was clearly oriented differently to the segment which contained it. Such features, which have been termed "channel faults" (16, 17), invariably made an angle of 70° with the twin boundary traversing the crystal, indicating that they were bounded by $\{111\}$ planes. The particle shown in Fig. 9d contains channel faults in both segments, although only one of these is clearly visible on the print (arrowed). The possible origin of these features, and of the twin boundaries themselves, will be discussed below.

About 3% of the particles in specimens sintered for 2 h appeared to contain two twin boundaries. Usually the two boundaries were parallel, as in the small particle shown in Fig. 9e and the larger one shown in Fig. 9f. In the latter case the particle has clearly experienced accelerated growth in a direction parallel to the twins, and is rod-like in shape; particles of this type were among the most common of the fast-growing structures. Very often such particles possessed slight notches where one of the twin boundaries intersected the surface (an example is arrowed in Fig. 9f). It seems very likely that these notches were responsible for the accelerated growth in one direction, since reentrant surface features of this type can act as preferential sites for the

nucleation of new atomic layers. Particles with two twin boundaries at an angle of 70.5° to each other were sometimes observed, and such particles also frequently exhibited abnormal growth. Figure 9g shows an example, and the thickness fringes in this particle indicate that the overall shape is approximately tetrahedral. Again, small notches can be seen (arrowed) where the two twins intersect the edge, and grooves are probably present along the length of the twin boundaries. Accelerated growth in directions parallel to these grooves would explain the shape of the particle.

Plate-like particles made up roughly 2% of the population after a 2-h heat treatment and these were often triangular in profile as in Fig. 9h. The plate-like shape could be demonstrated by tilting experiments; this is illustrated in Fig. 10. As noted in the Introduction, microdiffraction analysis has demonstrated that these particles contain twins parallel to the large faces (3, 7), and tilting experiments sometimes enabled these twins to be imaged directly. Occasionally the twins appeared to be associated with slight reentrant features, but these were difficult to image. Tilting experiments on larger plate-like particles revealed the reentrant features more clearly (see later).

Fewer than 1% of the particles in specimens sintered for 2 h exhibited the well-known decahedral structure, with five twin boundaries separating approximately tetrahedral segments. Figure 9i shows an example, and it is interesting to note that once again the particle possesses slight notches at the twin boundaries. Other workers have also observed reentrant features in decahedral particles (18), as well as in more complex multiply twinned particles with approximately decahedral structures (19). Recently Marks (20) has presented calculations which show that notching at the twin boundaries of decahedral particles produces a decrease in the overall surface energy, and is therefore thermodynamically favoured. It is probable that the reentrant

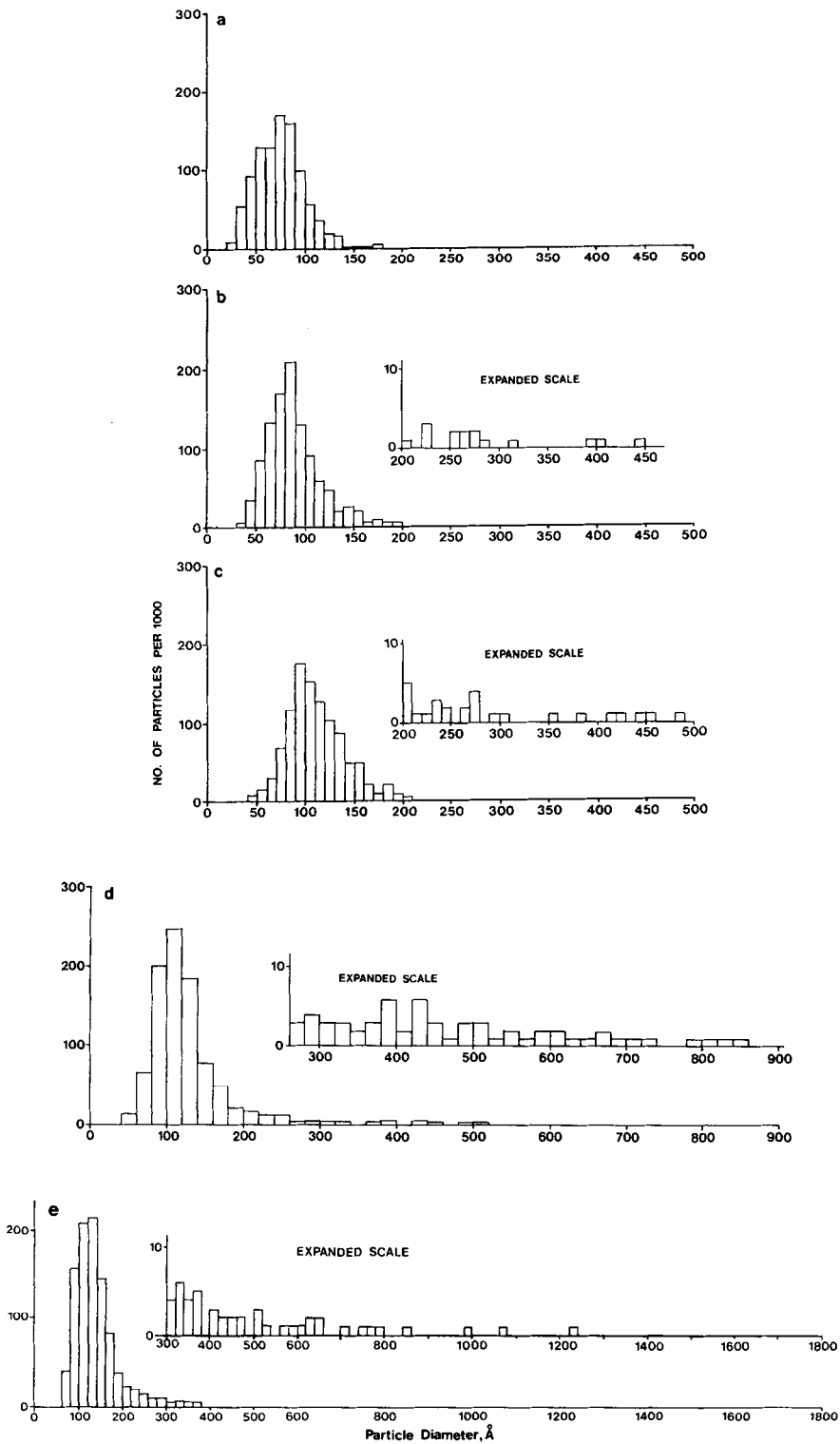


FIG. 7. Platinum particle size distributions for specimens heated in air at 700°C. Heated for (a) 10 min; (b) $\frac{1}{2}$ h; (c) 1 h; (d) 2 h; (e) 4 h; and (f) 8 h.

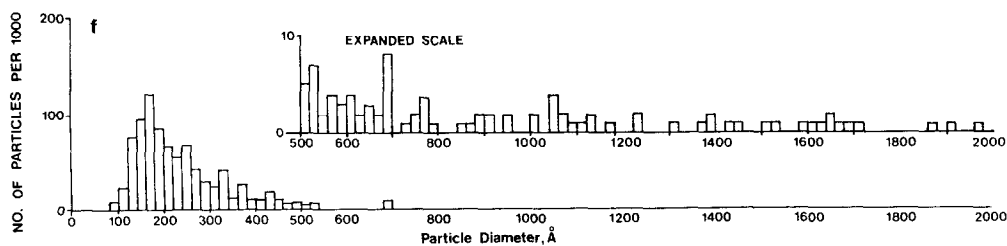


FIG. 7—Continued.

features observed in some of the other types of twinned particle described above could also be explained in terms of a minimisation of surface energy. In order to confirm this further theoretical work would be required.

Heat-treated in air at 700°C for 8 h. After 8 h the majority of particles were twinned. Again a wide variety of particle structures were observed, but the most common appeared to be the triangular plate and the needle. Occasionally the triangular plates were large enough to permit selected-area diffraction patterns to be recorded; Fig. 11 shows such a particle together with its diffraction pattern. Extra spots of the type $1/3\{422\}$ were invariably present in patterns recorded from plate-like particles, confirming that the particles were twinned.

Heat-treated in air at 700°C for 24 h. Only a few of these specimens were examined, but it appeared that the majority of

particles were very large triangular plates. Tilting experiments could easily be performed on these large particles, and often enabled the twin boundaries to be observed directly, as noted earlier. There always seemed to be two twin boundaries present, one of which was often clearly associated with a groove at the surface, as can be seen in the tilting sequence shown in Fig. 12. Like the reentrant features observed in the other structures described above, this groove can be explained in terms of a local minimisation of surface energy. It has been known for many years that the presence of two closely spaced parallel twin boundaries in fcc crystals can result in rapid plate-like growth (15), but to the author's knowledge it has not previously been possible to observe directly the groove responsible for this rapid growth. The fact that a groove was not *always* observed is not surprising since during growth the equilibrium structure would not always be maintained, a point which Marks has made in connection with decahedral particles (20). Thus the assumption by Cosandey *et al.* (7) that the absence of a macroscopic groove rules out the twin plane reentrant edge mechanism is incorrect.

The Formation of Twinned Particles

It has been shown that platinum particles in sintered catalysts exhibit five different twin boundary configurations: a single twin boundary; a single twin boundary plus one or more "channel faults"; two parallel twin boundaries; two twin boundaries at an angle of 70.5° and, in the decahedral structure, five twin boundaries. It has also been

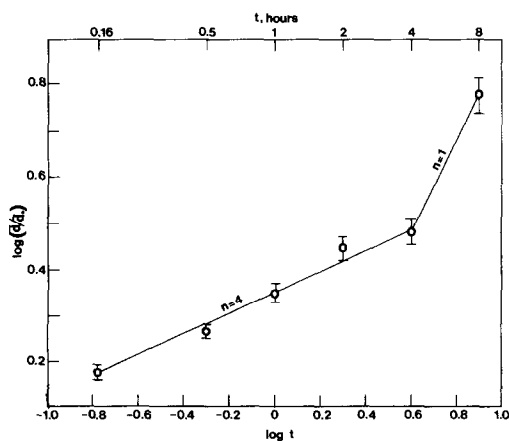


FIG. 8. Plot of $\log(\bar{d}/\bar{d}_0)$ vs $\log t$ for sintering in air at 700°C.

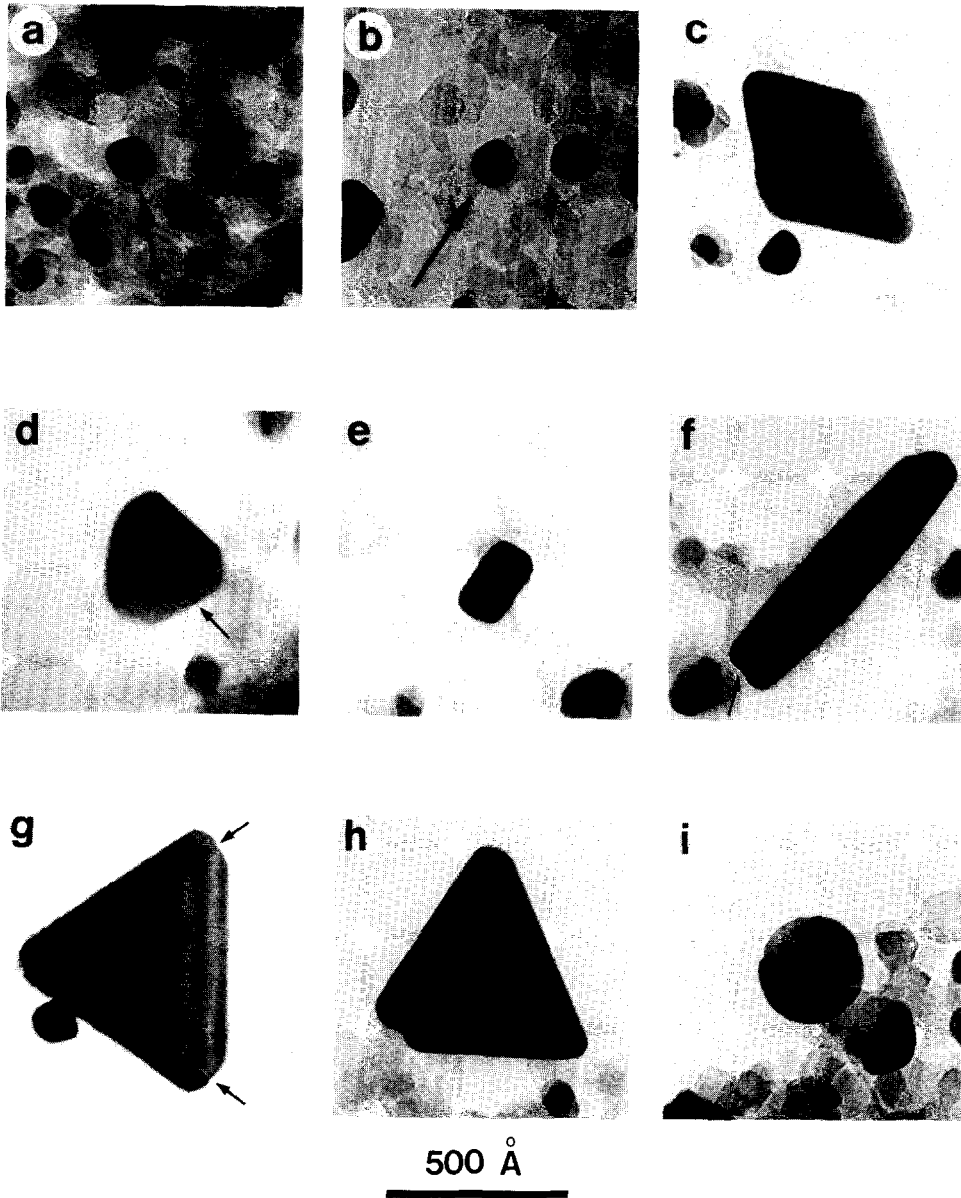


FIG. 9. Particle structures in specimens heated for 2 h at 700°C in air. (a) Single crystal octahedron; (b) small singly twinned particle; (c) large singly twinned particle (triangular bipyramid); (d) particle containing single twin boundary plus "channel fault"; (e) particle containing two parallel twin boundaries; (f) rod-like particle containing two parallel twin boundaries, with reentrant surface feature; (g) particle containing two twin boundaries at 70° to each other, with slight reentrant features; (h) triangular plate; (i) decahedron.

demonstrated that some of these configurations produce reentrant surface features which facilitate growth by the Ostwald ripening mechanism. However, the origin of the twin boundaries remains unclear. One

possibility is that twins arise as a consequence of particle coalescence. In support of this view, it is interesting to note the similarity of some of the twinned crystallites observed here to the structures reported by

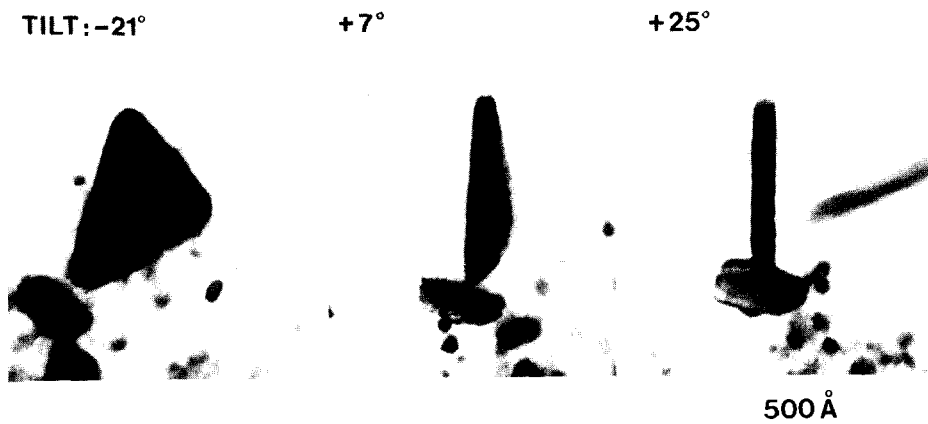


FIG. 10. Micrographs from a tilting sequence of plate-like particle in specimen heated for 2 h at 700°C.

McGinn *et al.* in their study of the coalescence of gold particles supported in a fused silica matrix (16, 17). These workers have demonstrated that coalescence can produce all of the twinned configurations listed above, with the exception of the decahedral structure. They have also proposed a model for twin formation, based on an earlier treatment of annealing twin formation by Gleiter (21), which satisfactorily explains the formation of these particles. This will now be summarised, although it should be stressed that other possible mechanisms exist. The model assumes that the coales-

cence of two single crystals results in a particle comprising two randomly oriented grains separated by a boundary. Migration of the boundary will occur by a net transfer of atoms from one grain to the other, the driving force being a reduction in overall boundary energy. Eventually this will result in the formation of a perfect $\{111\}$ plane across the advancing surface of the growing grain. Further migration of the grain boundary must occur one atomic layer at a time until the boundary migrates out of the particle. It is during this layer-by-layer growth process that the formation of a

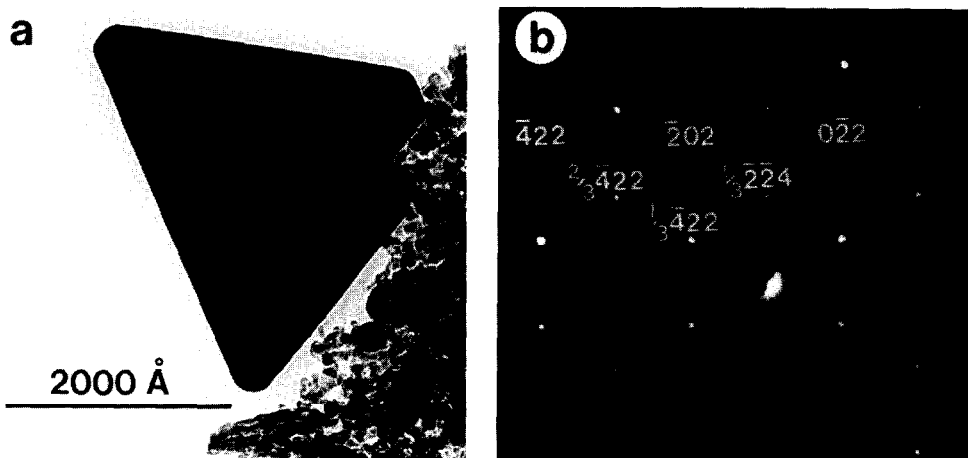


FIG. 11. (a) Triangular plate in specimen heated at 700°C in air for 8 h; (b) selected area diffraction pattern of particle.

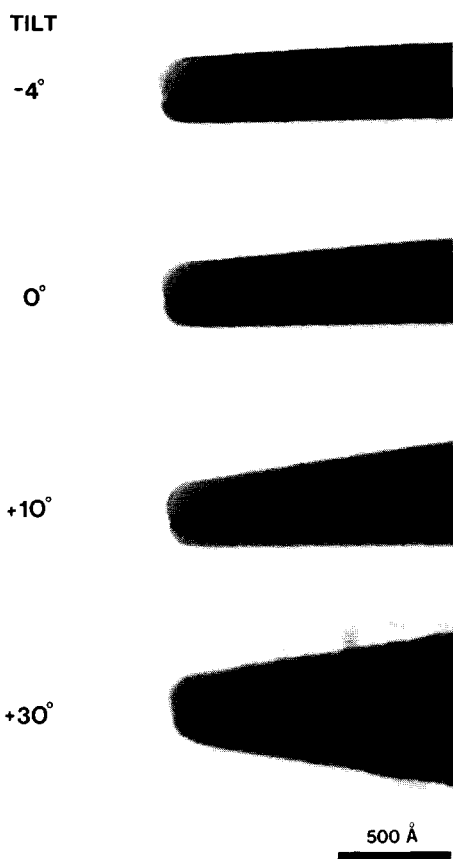


FIG. 12. Tilting sequence of very large plate-like particle in specimen heated at 700°C in air for 24 h. Shows presence of reentrant edge.

twin boundary or boundaries may occur, as a result of "errors" in the stacking sequence of newly deposited $\{111\}$ planes. In this way the coalescence of two single crystal particles could result in a single twin boundary or a series of parallel twin boundaries. Alternatively, of course, the grain boundary could migrate out of the particle without leaving any twins. McGinn *et al.* (16, 17) also consider the case of coalescence between a single crystal and a particle which already contains a twin boundary, and show that this could result in the formation of a new twin parallel or at 70.5° to the original one, or the formation of channel faults within the twin-related segments.

The only twinned particle which seems unlikely to have formed by coalescence is the decahedron. It is widely accepted that crystallites of this type originate from the very early stages of particle growth, when clusters with fivefold symmetry are energetically favoured (22). At later stages of growth decahedral particles would be unstable with respect to normal fcc structures, but it is not unusual to observe that some of them survive the growth process and reach relatively large sizes (23). Icosahedral particles, which are also thought to form during the early stages of growth, were not observed here.

CONCLUSIONS

This study, together with the earlier work (3), has shown that the sintering of supported platinum particles in oxidising environments is a highly complex process. It seems clear that both migration and coalescence and Ostwald ripening are involved, and it has been demonstrated that the growth rate of individual particles can vary considerably according to their structure. Because of this complexity, it has not always been possible to compare the sintering data with the predictions of theoretical models; instead, mechanistic insights have largely been obtained through a simple consideration of changes in the particle size distribution during sintering, and by analysing the structures of particles in heat-treated catalysts. The main conclusions of the present work can be summarised as follows.

1. The size distributions apparently indicate that migration and coalescence occurs for the smallest particles, but also show clearly that sintering becomes increasingly dominated by fast-growing particles, for which the growth mechanism is almost certainly Ostwald ripening. For the period 4–8 h, when the accelerated growth phenomenon strongly predominates, the sintering kinetics differ significantly from those of the earlier period.

2. Many of the fast-growing particles contained twin boundaries. It was frequently found that these boundaries were associated with reentrant surface features, which could be responsible for the accelerated growth by providing preferential nucleation sites. The formation of these features probably produces a reduction in the overall surface energy of the particles.

3. Most of the twin boundary configurations observed here could have formed during particle coalescence in the way described by McGinn *et al.* (16, 17). The features known as "channel faults" which were observed in some particles would appear to be particularly characteristic of a coalescence mechanism of twin formation.

Finally, one further point concerning the abnormally large particles should be made. It is clear from the micrographs shown in Figs. 4 and 5 that after 8 h at 700°C some of the platinum particles had grown to sizes in excess of the largest alumina pore size (i.e., >1500 Å). The question therefore arises of whether this type of particle growth could occur within the bulk of a real catalyst or whether growth above a certain size would be impeded by the alumina pores. Some recent TEM studies of platinum/alumina specimens prepared from the bulk catalyst do not appear to be in agreement on this point. Cosandey *et al.* (7) have observed large hexagonal and triangular plates (>2000 Å across) similar to those reported here in their sintered catalysts, while other workers have found that sintering produces irregular agglomerates of platinum whose shape is apparently influenced by the alumina pore structure (24, 25). Clearly further work is required in this area. However, it is worth pointing out that even if sintering within the bulk catalyst were restricted by the micropores, the growth of just a few abnormally large particles at cracks or macropores in the support structure, or on the surface of the support could still result in significant losses of available platinum surface area. Scanning electron microscope studies have shown that very large plati-

num particles can indeed grow on the surface of catalytic washcoats (26, 27).

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