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Particle Splitting and Redispersion Phenomena in Model Alumina-Supported Platinum Catalysts

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Transmission electron microscopy (TEM) has been used in an attempt to study the redispersion behavior of small platinum particles supported on flat, dense γ-alumina substrates. The alumina substrates were prepared both by anodizing and by sputtering techniques. A thin (1 to 2 nm) film of platinum was deposited onto these alumina substrates by sputtering. This film was subsequently transformed into discrete platinum particles by an initial heat treatment at 600°C for 18 hr in air, and then "redispersed" by heating at 500°C for 18 hr, also in an air atmosphere. Particle size measurements on TEM photomicrographs revealed no significant decrease in platinum particle size as a result of the "redispersion" heat treatment. These results are in contradiction to previous observations of platinum particle splitting under those conditions. The findings are discussed in the light of different concepts which have been used to explain redispersion phenomena.

INTRODUCTION

In 1960, McHenry and co-workers (*1*) noted an increase in the dehydrocyclization rate of *n*-heptane at 490°C, using alumina-supported platinum catalysts. This rate increase was attributed to an increase in the amount of soluble platinum which was believed to result from the formation of a $Pt/Al_2O_3/Cl$ type complex that increased the active surface area of the catalyst. This initial paper ignited interest in the subject that is continuing to the present day.

Since the work of McHenry *et al.*, several investigators, using different adsorption techniques, have observed an increase in platinum surface area in the temperature range 300–550°C for the platinum–alumina system (*2–9*). Numerous theories have been proposed to explain this phenomenon. In general, the models can be divided into two main categories. One category attributes the increase in surface area to the actual splitting of the particles themselves, while the other category invokes the formation and spreading of platinum monolayers on the substrate.

More recently, Ruckenstein and Malhotra (R&M) (*10*) noted a decrease of about 60% in platinum particle size by transmission electron microscopy (TEM), during heat treatment in air of particles supported on thin, dense, anodized alumina substrates. The samples were initially heat treated for 24 hr at 600°C and subsequently "redispersed" by heating for 24 hr at 500°C.

There has been fairly extensive study, over the past few years, of particle growth during heat treatment in air of model cata-

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FIG. 1(A). Sputtered specimen in open condition after 600°C coarsening heat treatment.

lysts, consisting of noble metal (or alloy) particles supported on thin, dense alumina films (*11–17*). No evidence for particle splitting was observed in those studies, but then the heat treatments in those cases were carried out at temperatures of 600°C or higher. In addition, the procedures for preparing the alumina films were different from those of R&M. Thus, it was of interest to see if particle splitting could be seen under the conditions reported by R&M using various alumina film preparation techniques. Our findings, which are contrary to those of R&M, are presented below.

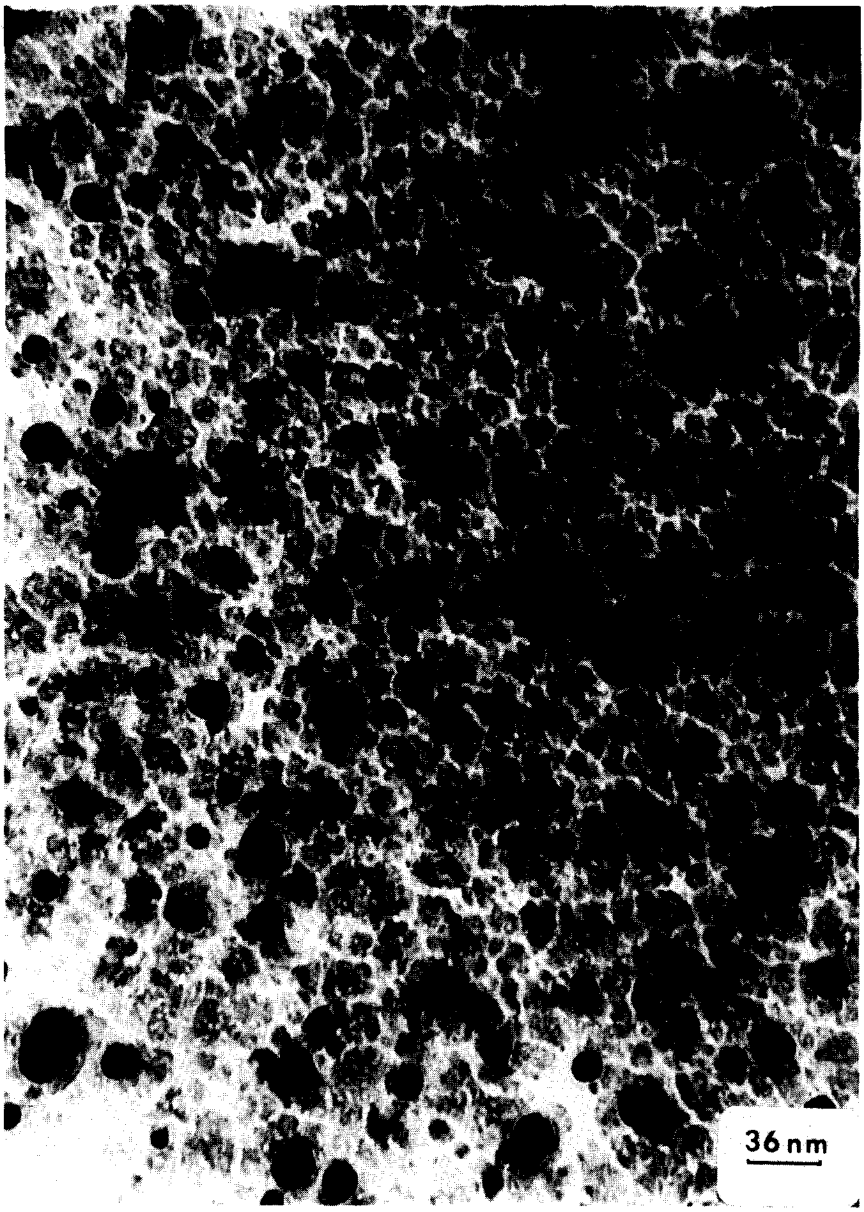

FIG. 1(B). Sputtered specimen in open condition after 500°C redispersion heat treatment.

EXPERIMENTAL PROCEDURE AND RESULTS

Two different types of alumina substrates were used in the experiments, sputtered substrates prepared by methods similar to those of Refs. (*11–17*), and anodized substrates similar to those used in Ref. (*10*).

The sputtered substrates were prepared in the following manner. About 20 nm of alumina was deposited on silica microscope slide, of dimensions 0.5 by 2.5 cm, by radio frequency sputtering in an argon atmosphere at a pressure of 25 Torr. Alumina films prepared in this way are relatively flat and dense. Next, thin films of platinum of either 1 or 2 nm thickness were sputtered onto the alumina under similar conditions. Up to six samples were prepared in this manner in a single batch. The specimens were checked for uniformity with a Joyce microdensitometer, and any samples which deviated by more than 10% in optical density were discarded.

The anodized-substrate samples were prepared in the manner described by R&M (*10*). High-purity aluminum foil was first chemically polished by immersion for 5 min at 80°C in a solution of 100 ml orthophosphoric acid, 5 ml nitric acid, and 20 ml distilled water. The polished foil was washed in distilled water and dried. Anodizing of the foil was performed at 15 V for 2 min in a solution of 3% tartaric acid with a pH adjusted to 5.5 by means of ammonium hydroxide. This produced an alumina film approximately 20 nm in thickness. The alumina was then heat treated at 600°C for 20 hr to transform it from the amorphous state to crystalline γ-alumina. Platinum was deposited, as described above, simultaneously onto two pairs of anodized-substrate and sputtered-substrate samples, for comparison purposes.

Three different types of experiments were performed. In the first experiment, sputtered-substrate samples with a 1-nm platinum deposit were heat treated either in an open silica dish exposed to laboratory air, or sealed in air in a silica capsule such that a pressure of one atmosphere was present at temperature. These two different means of controlling the sample environment were used in order to test one more difference in procedure between the work of R&M (*10*) and previous studies employing sputtered substrates (*11–17*). The specimens were placed in a furnace at 600°C for 18 hr. This initial heat treatment served a threefold purpose: (i) to transform the sputtered alumina to crystalline γ-alumina, (ii) to break up the thin film of platinum into particles, and (iii) to coarsen the platinum particles. The specimens were removed from the furnace and cooled to room temperature. Each specimen was broken into two halves. One half was investigated by TEM to establish the particle size obtained after heat treatment at 600°C, and the second half was retained for the redispersion treatment. The alumina film with its associated platinum particles was stripped from the first half of the silica microscope slide as follows. A drop of a solution consisting of 50% concentrated HF and 50% distilled water was placed onto the specimen surface. Within 2 or 3 min, the interface between the alumina film and the silica substrate was attacked, and it was possible to float off the alumina film and associated platinum particles by immersion of the specimen in a dish of distilled water. Samples were then removed from the bath onto copper microscope grids, dried, and examined by TEM. Figure 1A shows a typical micrograph of coarsened particles produced by heat treatment in an open dish at 600°C.

The second half of the specimen was heat treated at the redispersion temperature, 500°C, for 18 hr. After this second heat treatment, the specimens were air cooled, stripped from the silica support, and examined again by TEM to determine if particle splitting had occurred. Figure 1B is a typical electron micrograph of a specimen treated in the open condition after the redispersion treatment.

The average particle diameter from each sample was obtained by calculating the arithmitic mean from measurements of the diameter of a total of 400 to 800 particle projections on electron micrographs such as those shown in Fig. 1. Experimental error in particle size determinations can arise from two primary sources. The 10% tolerance in film uniformity can lead to an error in particle size of ±5%. The physical measurement of particle size on micrographs and the error associated with TEM magnification can give rise to a combined error of another ±5%. The resulting total error from these sources is estimated at about ±10%.

The fractional surface area of platinum particles covering the substrate was calculated assuming that each particle was hemispherical in shape, and expressing the total area of the particles as a percentage of the total substrate area. Since all particles were not perfectly hemispherical, the results of this calculation should be viewed as a convenient approximation to be used for comparative purposes only.

Table IA illustrates the results obtained from this first experiment. The decrease in particle size, from 12.2 to 11.0 nm, for the encapsulated samples is within experimental error and is certainly much smaller than the 60% decrease observed previously (*10*). The increase in particle size observed for samples heated in an open system is also within experimental error. In addition, there was no evidence for the increase in surface area covered by the platinum particles which should accompany any particle splitting phenomenon. Thus, we conclude that no particle splitting occurred in this experiment.

The second experiment was similar to the first with the exception that the initial platinum film deposited on the substrate was 2 nm in thickness and only the encapsulated condition was used during heat treatment. The purpose of this experiment was to investigate any possible dependence of particle splitting behavior on particle size. Table IB summarizes the results of this experiment. Again, the small decrease in particle size from 37.3 to 36.7 nm was within experimental error, and here also, no corresponding increase in the surface area covered by platinum particules was observed.

In the third experiment, both sputtered and anodized-substrate specimens were heat treated simultaneously in the open and the encapsulated environment. The anodized specimens were prepared for TEM in the following manner. Light scratches were made on the reverse side of the aluminum foils i.e., the side not coated with platinum, and the samples were immersed in a solution of 5% bromine, 1% distilled water, and 94% methanol. This solution dissolves metallic aluminum. Immersion was continued until a few holes appeared in the specimens. The specimens were then washed in distilled water and dried before examination by TEM. In the electron microscope, it was possible to observe pieces of the anodized film, and associated platinum particles overhanging the holes etched into the aluminum foil. Figure 2A is a typical micrograph of an anodized-substrate specimen heat treated in the open condition at 600°C for 18 hr. Figure 2B is a micrograph of the same sample after the 500°C redispersion treatment.

Table IC illustrates the results of this final experiment. No splitting of platinum particles was observed in any of the four samples. The increase in particle size, from

TABLE 1

Alumina substrate	System	After aging treatment			After redispersion treatment			Percentage change in diameter	Percentage change in Pt surface area
		Number of particles measured	Average diameter (nm)	Area of particles	Number of particles measured	Average diameter (nm)	Area of particles		
A									
Sputtered	Open	538	14.5	9.1%	573	15.0	8.6%	+3.4	−5.5
Sputtered	Closed	675	12.2	10.8%	650	11.0	8.7%	−9.8	19.4
B									
Sputtered	Closed	704	37.3	23.8%	700	36.7	21.2%	−1.6	−10.9
C									
Anodized	Open	588	11.0	22.5%	616	12.5	24.3%	+13.6	+7.0
Anodized	Closed	646	11.3	19.4%	870	11.3	22.9%	0	+15.3
Sputtered	Open	777	16.0	18.5%	559	14.9	17.0%	6.9	−8.1
Sputtered	Sealed	865	15.0	15.4%	360	17.9	16.0%	+19.3	+3.75

FIG. 2(A). Anodized specimen in open condition after 600°C coarsening heat treatment.

11 to 12.5 nm, observed for the case of the anodized-substrate specimen heated in the open condition, as well as the increase from 15 to 17.9 nm observed in the sealed sputtered-substrate specimen, are consistent with the size distribution data presented below. Figures 3 and 4 are plots of the number of particles of a given size versus particle diameter. Figure 3A was obtained from the sputtered substrate specimen heat treated in the open condition at 600°C for 18 hr, while Fig. 3B shows data from the sample after the redispersion treatment. Similarly, Figs. 4A and B show results obtained before and after the redispersion treatment from the anodized-substrate sam-

FIG. 2(B). Anodized specimen in open condition after 500°C redispersion heat treatment.

ple heated in the open condition. The most significant feature of these bell-shaped curves is that after the redispersion treatment, curves 3B and 4B have developed tails at the large particle end of the distributions. This is another indication that the large platinum particles are increasing in number and, hence, that particles are coarsening rather than splitting into smaller particles.

We must thus conclude that the present investigation of redispersion in model γ-

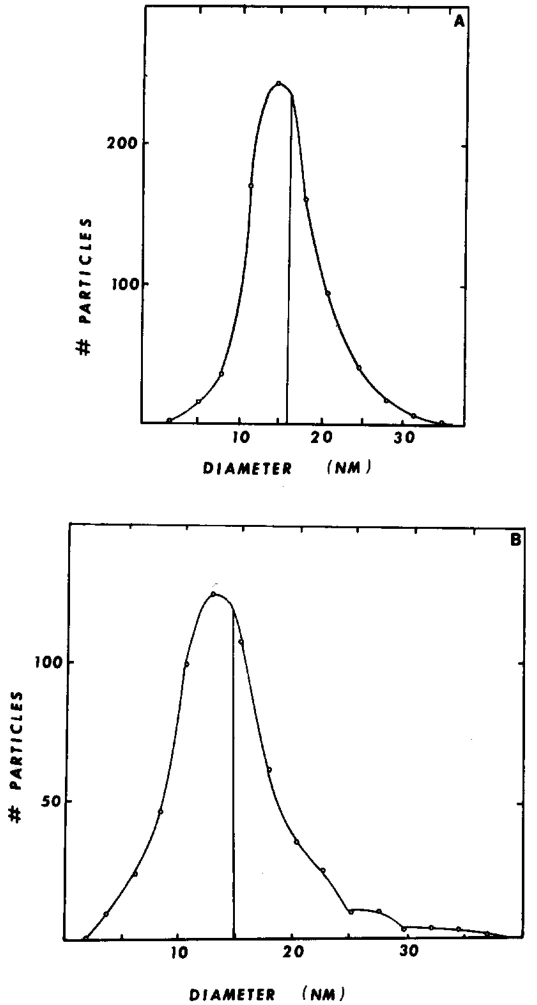

FIG. 3(A). Data obtained from sputtered specimens in the open condition after 600°C coarsening heat treatment. (B) Data obtained from sputtered specimens in the open condition after 500°C redispersion heat treatment.

alumina supported platinum catalysts yields no evidence to support the hypothesis of redispersion by particle splitting.

DISCUSSION

As mentioned earlier, redispersion of γ-alumina supported Pt catalysts, in oxygen, has been explained by using one of two different general concepts. One concept has attributed the increase in surface area to a physical splitting of the supported particles (*10*), while the other has invoked the formation of various types of two-dimensional platinum dispersions (*1–8*). It is clear from the most recent work (*8, 18*) that a critical temperature range for redispersion exists in the vicinity of 500 to 600°C. Maximum redispersion occurs in samples heat treated near the middle of this range, whereas surface area loss results from heating at or above 600°C. Also, it has been pointed out (*8, 10*) that this critical temperature range corresponds approximately to the decom-

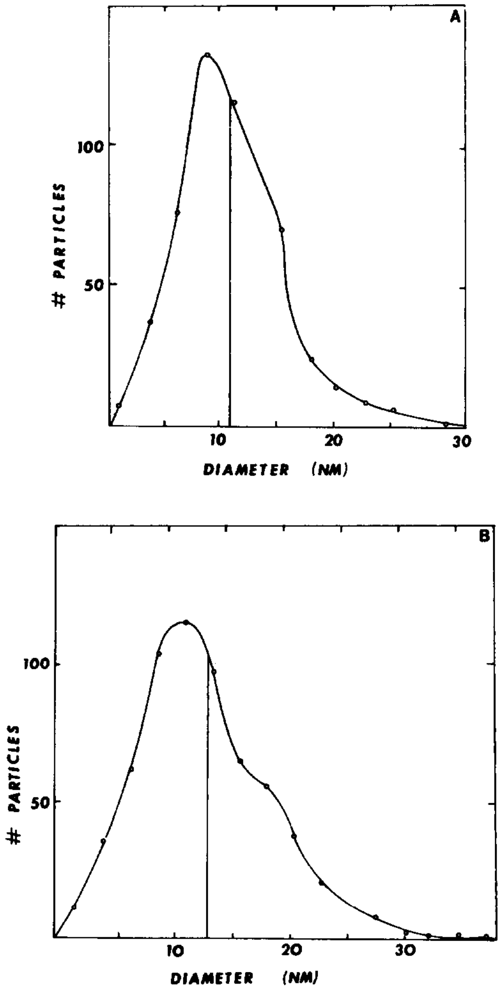

FIG. 4(A). Data obtained from anodized specimens in the open condition after 600°C coarsening heat treatment. (B) Data obtained from anodized specimens in the open condition after 500°C redispersion heat treatment.

position temperature of solid platinum oxides in air (~550°C). Thus, independently of the particular concept employed to explain redispersion, one may conclude that the stability of platinum oxide is crucial to the redispersion process.

In both the experiments of R&M (*10*) as well as in our present experiments, the experimental systems were model catalysts which contained a much higher metal loading than commercial catalysts. In spite of the high metal loading, however, these model systems are quite adequate to address the hypothesis of redispersion by particle splitting which is the only issue addressed in this paper. R&M (*10*) observed a splitting of 11-nm particles to 4 nm when samples heat treated in air at 600°C (in which the platinum was presumably present in metallic form) were subsequently treated at 500°C (thus presumably converting the particles, at least partially, to platinum oxide). R&M speculated that the splitting was due to fracture induced by a build-up of strain energy associated with the formation of a "platinum–alumina complex." While such a mechanism is conceivable, the minimization of the system free energy demands a trade-off between relaxation of strain energy (a particle volume dependent quantity) and the creation of new surface area. In this type of problem, it is possible to define a critical particle size below which the critical event (in this case fracture) will not occur; hence, in general, the probability of particle splitting will diminish with decrease in particle size. Unfortunately, the properties of platinum oxide (or of R&M's complex) are not sufficiently well-known to allow an estimate of the critical particle size for fracture. But the fact that redispersion has been observed in catalysts with dispersions of 0.3 to 0.4 (*4*, *8*), corresponding to rather small particle sizes of about 3 nm, may be viewed as evidence against the concept of particle splitting. Furthermore, there is no simple way of telling whether in fact any significant strain energy would build up during the conversion of a platinum particle to platinum oxide, since a resolution of this issue would require detailed knowledge of the oxidation process. For example, oxide films forming on metals, with significant volume change, will frequently grow without fracturing because the build-up of strain energy can be relaxed by certain modes of growth.

However, let us assume for the sake of argument that strain energy can build up. The meager information on platinum oxide indicates that an increase in volume would result in oxidation (*19*). Thus, a platinum particle undergoing oxidation on an alumina substrate would presumably be constrained from expanding by its interface with the alumina. The particle would therefore develop a compressive state of stress while the substrate would build up a balancing state of tensile stress. Under those circumstances, it would be most likely for fracture, if it occurred, to take place within the alumina substrate rather than in the particle.

On balance, there does not appear to be any compelling reason to accept R&M's particle fracture hypothesis. The results of our present experiments show that the particle splitting observed by R&M is by no means a universal phenomenon. However, any attempt on our part to find reasons for their observations of particle splitting would amount to mere idle speculation.

We now turn to the concept of redispersion via the formation of a two-dimensional platinum phase. Several investigations of γ-alumina supported transition metal oxides have determined that these oxides can exist in two forms, a bulk phase and a two-dimensional phase. Examples include chromium (*20*), cobalt (*21*), rhenium (*22*), and rhodium oxides (*23*). Evidence for similar behavior in the case of γ-alumina supported platinum has very recently been provided by Yao *et al.* (*24*). It has been shown that for surface concentrations below some critical surface coverage, all of the above supported transition metal oxides exist in the form of a two-dimensional dispersed phase, in which each ion is available to chemisorption. For large surface coverages, the excess oxide exists in the form of a three-dimensional or bulk phase, which is in equilibrium with the critical concentration of the two-dimensional phase.

Yao *et al.* (*24*) have proposed that redispersion of Pt supported on γ-alumina can be understood by the formation of such a two-dimensional phase, which they find can cover up to ~10% of the surface of the support at saturation, but which can exist only at temperatures where platinum oxide is stable. Thus, when a Pt/Al_2O_3 catalyst is heated either under reducing conditions, or in an oxygen containing environment but at temperatures above the decomposition temperature of platinum oxide, the platinum will be present primarily in the metallic state, and any individual platinum atoms will quickly agglomerate into particles. If this same catalyst is then treated in air at, say, 500°C, some platinum oxide will form and eventually spread on the surface to cover up to 10% of the substrate, thus leading to the phenomenon of redispersion. In the presence of excess platinum, such that a bulk oxide is also present, some surface area loss could continue to be observed after redispersion, as a result of the coarsening of the bulk phase. A generally similar description of the redispersion phenomenon has been given by Fiedorow and Wanke (*8*) and Baker (*9*).

The above picture is consistent with the majority of observations of redispersion by chemisorption techniques, as well as our present results. The mean platinum coverage in the present samples was 1 nm or more, corresponding to about six or more monolayers of platinum. Thus, the transfer of 10% of a monolayer from the particle phase to the two-dimensional phase during the redispersion treatment would hardly be detected. The absence of any significant increase in particle size during heat treatment at 500°C, which would be expected if platinum particles were converted to a lower density platinum oxide, might indicate that the kinetics of oxidation of 11 nm or larger platinum particles are rather slow at that temperture.

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