

The Equilibrium Shape and Surface Energy Anisotropy of Clean Platinum

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We have measured the equilibrium shape of clean platinum by monitoring the changes in the shape of a series of micrometer-sized platinum droplets during annealing at 1200°C in 10^{-7} Torr of oxygen. The droplets start out with a rounded shape and a wavy surface. Upon annealing for 24 h or more, the particles are converted to nearly spherical shapes with distinct facets in the (100) direction and smaller facets in the (111) direction. At equilibrium, the facets only cover 16% of the particle's surface. The rest of the surface is stepped or kinked. The equilibrium particle shape is also independent of particle size for particles in the size range explored here ($d > 1$ micrometer). Initially, the particles show a series of hill and valley structures around the (100) facets. However, the hill and valley structures disappear after a long anneal. After a long anneal, the particles also assume an epitaxial relation with the support. From the data, we estimate that the surface energy of platinum only varies by about 92 erg/cm² with crystal face, with Pt(100) having the lowest surface energy, Pt(111) having a slightly higher surface energy, and all of the other faces of platinum having essentially the same surface energy. By comparison, previous workers have shown that heats of adsorption of simple gases often vary by 350 erg/cm² with crystal face. The implication, therefore, is that in platinum the variations in surface energy with orientation are small enough that particle shape control in supported metal catalysis is feasible. Consequences to the stability of various single crystal faces are also discussed. © 1990 Academic Press, Inc.

INTRODUCTION

The equilibrium shape and energy anisotropy of metal crystals has been studied for over 100 years. The theory of equilibrium crystal shapes stretches back to work of Gibbs and Curie in 1885 (1). The Wulff construction to determine equilibrium crystal shapes was first proposed in 1901 (2). Given that long history, it is surprising how few detailed measurements of equilibrium crystal shapes of clean metal crystals appear in the literature. In the middle to late sixties several papers appeared which reported

equilibrium crystal shapes and surface energy anisotropies for gold, silver, nickel, copper, and iron (3-5). Unfortunately, none of these measurements were done under what would now be considered to be clean conditions. Dreschler (6) has argued that the crystal shapes in all of the measurements prior to 1980 were strongly perturbed by the presence of an unknown monolayer on the crystal's surface. As a result, he concluded that all of these measurements were inaccurate. In the recent literature, there have been measurements of the equilibrium shape of gold, lead, and indium (7-10). Unfortunately, there have not been any reports of the equilibrium shapes of metals which would be interesting to catalysis.

Here, we examine the equilibrium shape of micrometer-sized platinum particles. Our interest in this problem arose because we were trying to understand how we could

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control particle shapes in a supported platinum catalyst (21). However, in order to interpret the data, we needed to have accurate measurements of the surface energy anisotropy and equilibrium crystal shape of clean platinum. Many years ago, McLean and Mykura measured the surface energy anisotropy of clean platinum (11) using the twin boundary grooving technique. However, these data were not taken under what would now be considered clean conditions. We are not aware of any equilibrium shape measurements. Thus, there was a need to measure the equilibrium shape of clean platinum.

EXPERIMENT

Our experiment was to deposit droplets of platinum onto a substrate, and then heat the substrate in an ultrahigh vacuum system at 1200°C and wait for the particle shape to equilibrate. Periodically, samples were removed for analysis with a Hitachi Model S 800 scanning electron microscope (SEM). Sample cleanliness was examined by reannealing samples in a PHI 660 scanning auger microprobe (SAM).

The droplets were made by loading a piece of high-purity platinum wire in a tungsten basket in a vacuum system, and rapidly heating the basket so that the platinum wire explodes. The procedure yields particles with a wide size distribution. The size distribution has never been completely reproducible, however.

We found that even at 5×10^{-10} Torr, our sample slowly accumulated carbon from the background. Therefore, in all of the work here, we pressurized the chamber with oxygen. A typical oxygen partial pressure was 1×10^{-7} Torr. We adjusted the oxygen partial pressure so that there was sufficient oxygen to burn off all of the carbon and yet keep the oxygen partial pressure low enough so that we could not detect oxygen on our sample using Auger electron spectroscopy (AES). Oxygen desorbs from platinum at about 700°C. As a result at 1200°C, the oxygen concentration on the particles should be

rather low. Shi's model (22) predicts that under the conditions used here, the adsorbed oxygen should only change the surface energy of the individual faces by 0.1 erg/cm² or less. This is a small change compared to the variation in the surface energy with orientation measured below. Admittedly, we would not have detected 1–2% of a monolayer of oxygen with AES. Two percent of a monolayer of oxygen would change the surface energy anisotropy by 35 erg/cm² which is starting to be significant. Thus, from the AES measurements alone, we could not be sure that the surface oxygen concentration was low enough to have a negligible effect on the equilibrium shape. However, we have found that we can change the oxygen partial pressure by plus or minus a factor of two or three and it has a negligible effect on the equilibrium shape even though, at our conditions, a factor of two change in the oxygen pressure produces a factor of two change in the surface oxygen concentration. Thus, we conclude that the oxygen is cleaning the particles. However, there is insufficient oxygen on the particles to have an important effect on the equilibrium shape. As a result, one can measure the equilibrium shape of clean platinum in the presence of 10^{-7} Torr of oxygen at 1200°C. The oxygen also has the secondary effect of promoting surface mobility which allowed us to measure equilibrium shapes at lower temperatures.

We have done measurements using a number of oxide substrates. However, we found that when we rapidly heat and cool the substrate during our sample preparation procedures, the substrate would crack. Then small pieces of substrate would migrate onto our platinum particles. An example of this is given in Fig. 1. The presence of oxide particles on the substrates complicated our analysis procedure. As a result, we decided to switch to a platinum foil substrate. Platinum wets platinum so if one simply evaporated a platinum droplet onto a clean piece of platinum foil and then annealed, the platinum droplet would spread

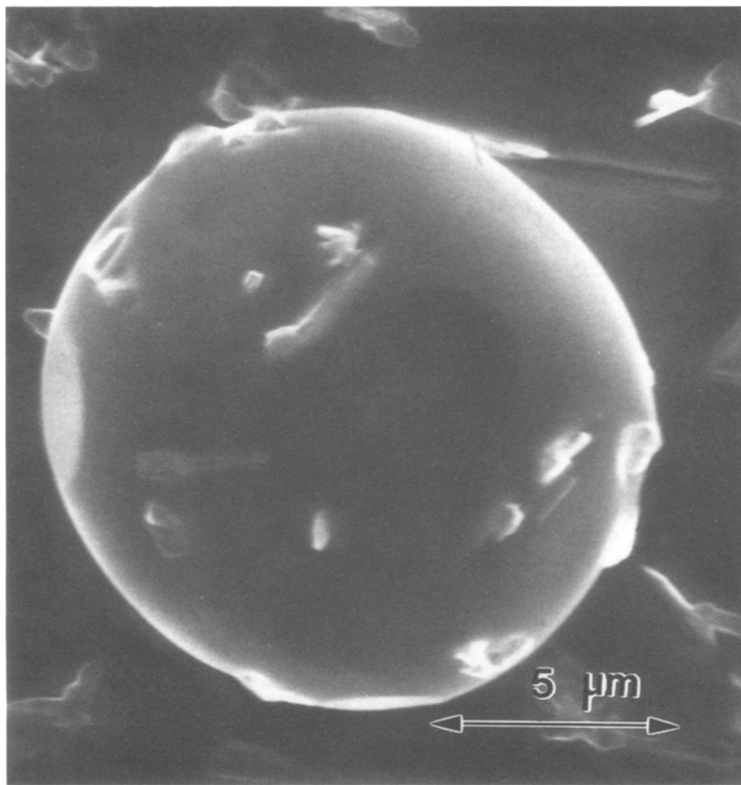


FIG. 1. A micrograph of a particle in a platinum on alumina catalyst prepared by evaporating platinum droplets onto a supported alumina film, sequentially heating to 1200°C for 24 h, cooling, and heating again. The crystalline chunks on the particle are pieces of alumina which have migrated onto the particles during the heating and cooling process.

uniformly over the surface and disappear. However, when a commercial piece of platinum foil is heated in an oxygen atmosphere, a thin oxide layer forms over the surface of the foil due to silicon migration from the bulk of the foil. We found that when we evaporated platinum droplets onto this oxide layer the platinum droplets bead up. We did not detect silicon or silica migration onto the droplets with Auger. As a result, we could deposit platinum onto an oxide substrate and not have a problem with the oxide migrating onto the platinum particle.

We have also measured channeling and back-scattered electron patterns on our particles to determine their crystallinity and orientation. The majority of our channeling measurements were performed on the JOEL

JSM 35-C scanning electron microprobe. In channeling, a beam a few hundred nanometers in diameter was rocked about a 30- μm disk either on or directly above the sample. The resulting channeling pattern was recorded photographically. We also conducted some channeling measurements with a Zeiss DSM-940 scanning electron microscope. The beam was rocked about a point directly above the sample and a channeling pattern was recorded. The channeling measurements were all confirmed by back-scattered electron diffraction measurements on the JOEL JSM 35-C. In the later measurements a 0.3- μm beam was focused onto the particle at an incident angle of about 70° and the resultant diffraction pattern was recorded photographically.

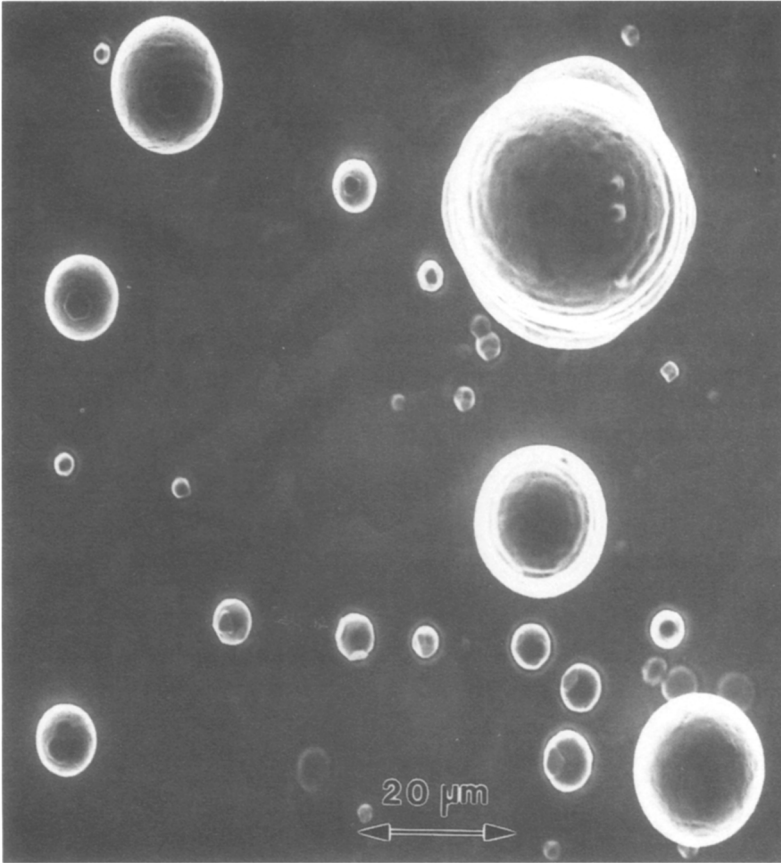


FIG. 2. A micrograph of some of one of our platinum or platinum/silica samples just after deposition.

RESULTS

Figure 2 shows a low magnification scan of particles immediately after deposition. We observe a wide distribution of particle sizes. Most of the particles look like drops which have frozen upon impact with the surface. There are also waves on the surface of the particles. Higher magnification pictures show that the base of the particles does not conform to the support. Rather, the particles seem to be frozen so that they span a series of small hills in the substrate; there are gaps between the particles and the support in the area between the hills. There are also waves in the surface on each of the particles which appear to be associated with the impact process. No facets are seen in

the particles in Fig. 2. However, we have occasionally observed facets in some of our other samples. Surprisingly, the facets are not oriented in any particular direction.

When we anneal the samples for a day or more at 1200°C , most of the particles smaller than about $0.1\ \mu\text{m}$ disappear while larger particles assume a general spherical shape. Figure 3 shows how the particle shape evolves in time for one of the $15\text{-}\mu\text{m}$ particles. The particle starts out as a drop with a wavy surface. However, when the sample is annealed for 24 h at 1200°C , the particle assumes a generally spherical shape with a series of distinct facets of different sizes. There also are a few large defects in Fig. 3 which are a result of small pieces of platinum which have not merged with the bulk. From

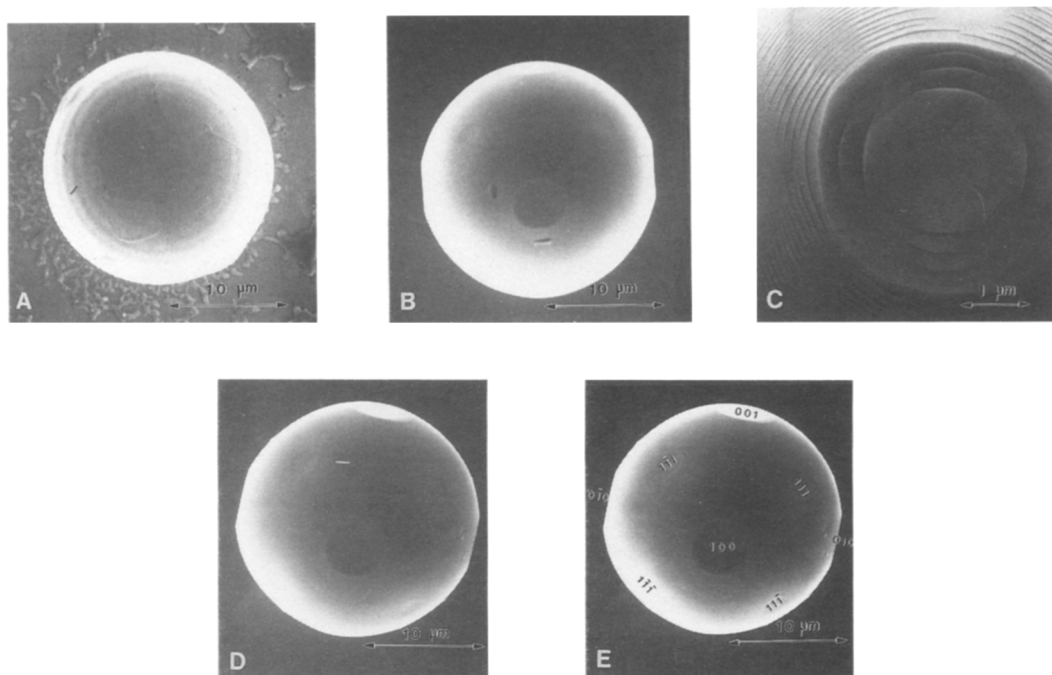


FIG. 3. A series of micrographs of a 15- μm platinum particle (a) just after deposition, (b) after being annealed for 24 h at 1200°C in 10^{-7} Torr of oxygen, (c) a higher magnification picture of the (100) region of the particle in b, (d) the same particle after being annealed for an additional 48 h (i.e., 72 h total) at 1200°C in 10^{-7} Torr of oxygen, (e) labeled version of the picture in d.

the distribution and symmetry of the facets one would assume that the larger facets lie along the (100) directions, while the smaller facets lie along the (111) directions. These assignments were confirmed with the channeling measurements described below. Thus it seems that upon annealing, our particles assume a basically spherical shape with distinct facets in the (100) and (111) directions.

We have examined the particle in Fig. 3b at a much higher magnification. Figure 3c shows an enlargement of the region near the (100) facets on this particle. Note that after a 24-h anneal, the (100) facets are not distinct planes. Rather, there are a series of waves in the particles surface. Such shapes have been seen in other crystal systems and are called "hill and valley structures" (16). We have examined the evolution of the hill and valley structures with time. Generally, we

find that the hill and valley structures slowly shrink as we anneal the sample; eventually, the hill and valley structures disappear. The final particle shape is given in Fig. 3d. The particle is still spherical, and there are still distinct (100) and (111) facets. The final shape is stable. Therefore, we believe it to be the equilibrium shape. Figure 3e is included to indicate the orientation of the facets on the particle.

Figure 4 shows how the particle shape evolves for a larger particle. The results are similar to those in Fig. 3. We start with particles that look like droplets frozen on the surface. After a 24-h anneal, the particle assumes a spherical shape with hill and valley structures in the (100) direction and small dimples in the (111) direction. The hill and valley structures slowly shrink with additional annealing. However, the hill and valley structures are still visible at high reso-

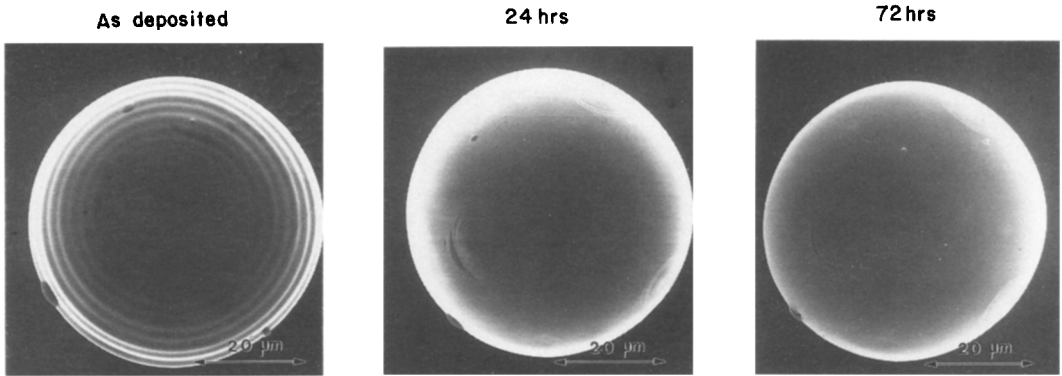


FIG. 4. A series of micrographs of a larger platinum particle (a) just after deposition, (b) after being annealed for 24 h at 1200°C in 10^{-7} Torr of oxygen, (c) after being annealed for an additional 48 h (72 h total) at 1200°C in 10^{-7} Torr of oxygen.

lution even after a 168-h anneal. Still, if we extrapolate our data to long times, it seems that the hill and valley structures will eventually disappear. We will then be left with a particle which has a shape which is self-similar to the shape in Fig. 3d.

The results in Figs. 3 and 4 are typical for our particles. However, there are exceptions. For examples, Fig. 5 shows the time evolution of a double particle formed when a drop of platinum splatters onto a previously formed platinum particle. We find that initially the two drops evolve somewhat independently. However, the larger drop slowly

grows at the expense of the smaller drop. The result is that we get some complex structures which change with time. The shapes of the double particles do not stabilize within the time scale of our experiment (1 week). Therefore, we do not believe them to be equilibrium shapes.

We have made measurements similar to those in Figs. 3–5 on several different samples. We have found that the final shapes of all of our sample particles larger than $1 \mu\text{m}$ are self-similar to those in Figs. 3 and 4. The double particles have random shapes. The particles smaller than $1 \mu\text{m}$ disappear or ag-

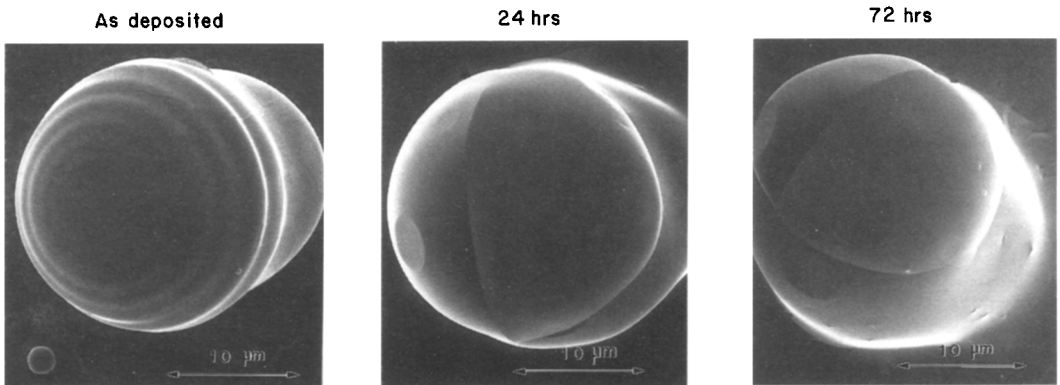


FIG. 5. A series of micrographs of a double particle formed when one platinum droplet was evaporated onto a second one (a) just after deposition, (b) after being annealed for 24 h at 1200°C in 10^{-7} Torr of oxygen, (c) after being annealed for an additional 48 h (72 h total) at 1200°C in 10^{-7} Torr of oxygen.

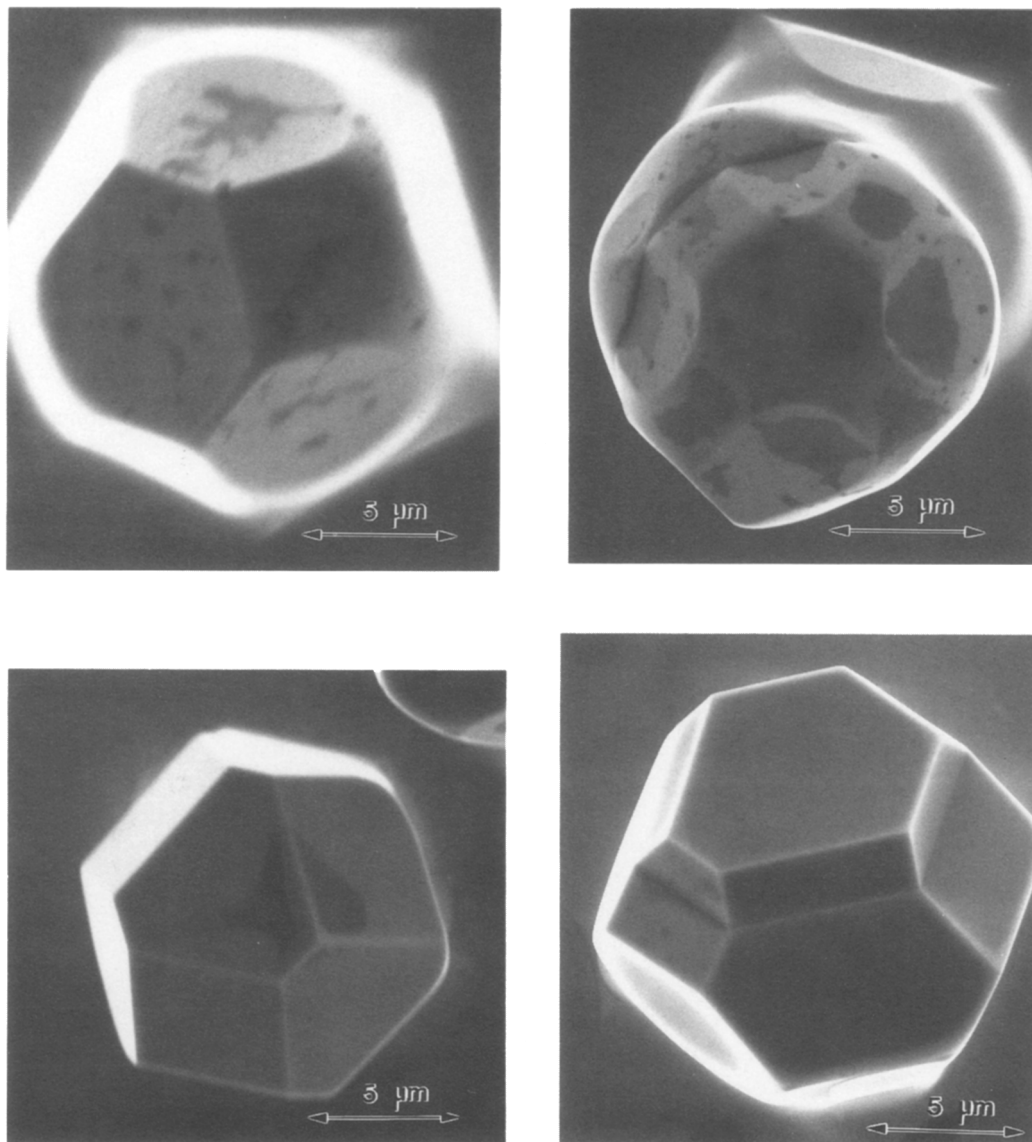


FIG. 6. Micrograph of some carbon-covered particles. The particle on the top left was formed by annealing in "vacuum." The other particles were formed by annealing to 1300°C in 5×10^{-8} Torr of oxygen. (Carbon is not removed under these conditions.) Auger indicates that all of these particles are heavily contaminated with carbon.

glomerate. The observation that upon equilibration all of the particles in multiple samples reach the same final shape is further evidence that this final shape is the equilibrium shape of clean platinum.

Dirty platinum looks different, however. For example, Fig. 6 shows pictures of some carbon covered particles. The particles look

like a classic cubo-octahedron with large (111), (100), and (110) facets and curved boundaries. There is also a series of distinct dark spots on the faces of the particle. AES indicates that the dark spots are composed of carbon layers so thick that we cannot detect platinum. There is carbon on the bright areas of the particles too. However,

in the bright regions the carbon is only a few layers thick. Generally most or all of the particles in our heavily carbon contaminated samples looked like cubo-octahedrons. However, we have only detected cubo-octahedrons when the sample was heavily carbon contaminated. Once we cleaned the sample, the shape always reached that in Fig. 3d upon equilibration. Therefore, we conclude that in our samples, a cubo-octahedron is characteristic of a carbon-contaminated particle. It is unclear whether other contaminants could also produce cubo-octahedrons.

We have also examined our samples with a scanning auger microprobe (SAM) to insure that we are measuring the equilibrium shape of clean platinum. If we start with a freshly prepared sample which has been treated in oxygen and load the sample into the SAM, we find the surface is always contaminated with carbon during transfer. However, that carbon can be removed either by light sputtering or annealing for a few minutes in oxygen at around 1200°C. In contrast, at the end of our SEM measurements, the surfaces of the particles are always covered with multilayers of carbon. Most of that carbon is removed when the sample is annealed for 1 h in 10^{-7} Torr of oxygen. However, we needed to lightly sputter one edge of the sample and then heat the sample for 3h more in 10^{-7} Torr of oxygen to remove the remainder of the carbon from the sample. The particles remained clean upon further annealing in 10^{-7} Torr of oxygen. There was oxygen (from SiO) on the support; however, no oxygen, carbon, or other impurities could be detected on the particles. We also could not detect any shape change during the annealing process. While the resolution of the SAM is lower than that of the SEM, the particles continue to show a generally rounded shape, with distinct (100) facets of the size given in Fig. 3d. There were also smaller (111) facets in our best SAM pictures. However, they were not clearly resolved. We cannot exclude there being some

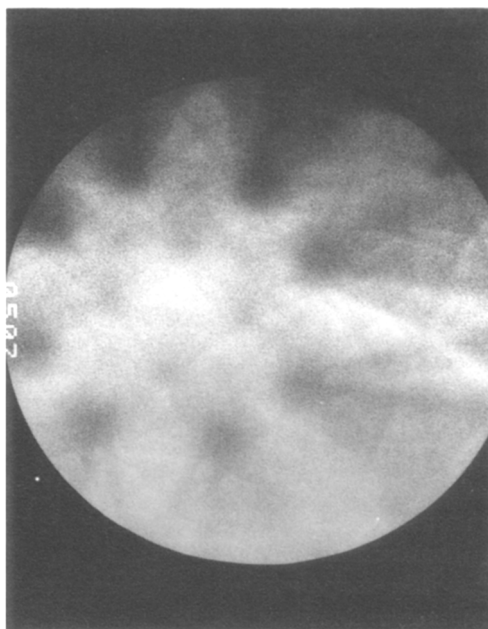


FIG. 7. A channeling pattern of one of our particles. The channeling pattern was taken by tilting the sample so the electron optical axis lies approximately perpendicular to one of the large facets on the particles and rocking the beam about a 30- μ m disk on the particle.

traces of impurities on our particles which could not be detected with our SAM. However, the best available evidence is that the shape in Fig. 3d represents the equilibrium shape of clean platinum.

Finally, we have done channeling and back-scattering measurements on the particles described above to try to confirm the orientation of our facets. Figure 7 shows a channeling pattern taken after tilting the sample so that one of the large facets on one of the particles was approximately perpendicular to the electron axis in the incident beam. Note the square pattern in the figure. It is characteristic of the channeling pattern from a (100) face in a FCC material. The channeling pattern is a classic FCC pattern. There is no evidence for twinning or other defects. Therefore, we have concluded that the particle is a single crystal, and the large facet is a (100) plane. The (100) axis is off the center of the image in Fig. 7 because

we could not align the face of the particle exactly with the incident beam. The difference corresponds to an angle of 3° .

We observed similar patterns for all of the individual particles we examined. (The double particles give different results). Therefore, we conclude that the single particles are single crystals. We also conclude that the larger facets are (100) planes and the smaller facets are (111) planes, as expected from their geometry.

We have also confirmed the orientation and crystallinity of the particles with back diffraction. Figure 8 shows a back diffraction pattern taken on a different particle than the one used for the measurements above. Again, it is a classic FCC pattern with no evidence for twinning or other defects. The orientation of the pattern is as expected if the large facets on the particle are (100) planes and the smaller facets are (111) planes. This is further evidence that the particles are single crystals, and the faces are distinct (100) and (111) planes.

The channeling and back diffraction patterns in Figs. 7 and 8 were taken using a beam centered on the sample. We have also taken channeling patterns by rocking the beam at a point just above the particles in one of our samples. When you rock the beam above a particle it is possible to measure separate channeling patterns for the particle and the support simultaneously, as shown in Fig. 9. In Fig. 9, the channeling pattern in the center of the photograph comes from the particle. The channeling pattern along the edges of the photo comes from the support. Note that the channeling pattern from the particle exactly lines up with the channeling pattern with the support. Therefore, we conclude that the crystallographic axis of the particle is exactly aligned with the crystallographic axis of the support.

We have only done the off-particle rocking curves (i.e., channeling patterns) for a few of our particles. However, we have made many more measurements where we compared the channeling pattern from our

particles and the channeling pattern from the support. As a result of these measurements we conclude that the particles start out with no special orientation with the support. However, upon annealing for 72 h at 1200°C , the particles rotate so that their crystallographic axis is aligned with the crystallographic axis of the support.

DISCUSSION

Looking back at the data, we find that at equilibrium, platinum assumes a basically spherical shape with distinct (100) and (111) facets, and curved regions in between. The shape appears to be independent of particle size, i.e., the shapes are self-similar. Basically spherical shapes have been predicted theoretically (12–17). They also have been observed for gold particles (7) which had been annealed at high temperatures. Hence, such shapes are not totally unexpected. Still, the fact that platinum assumes a rounded shape and is not simply a cubo-octahedron may surprise some readers.

The idea that equilibrium shapes of metals are cubo-octahedrons comes from old measurements (3). These measurements are now thought to be characteristic of contaminated samples (5). We have observed cubo-octahedrons when our samples were heavily contaminated with carbon. However, we have not observed any cubo-octahedrons once our particles were clean. Our particles do look somewhat like cubo-octahedrons with a transmission electron microscope (TEM). However, the SEM measurements show clearly that they are not cubo-octahedrons. Thus, we conclude that at equilibrium clean platinum assumes a rounded shape with distinct (100) and (111) facets and curved regions in between. There is no evidence for cubo-octahedrons.

One interesting feature in our data is that on clean platinum, the facets cover a relatively small fraction of the particle's surface. Theoretically, equilibrium particle shapes are determined by the variation in the surface free energy with orientation. A liquid drop is spherical because there are no

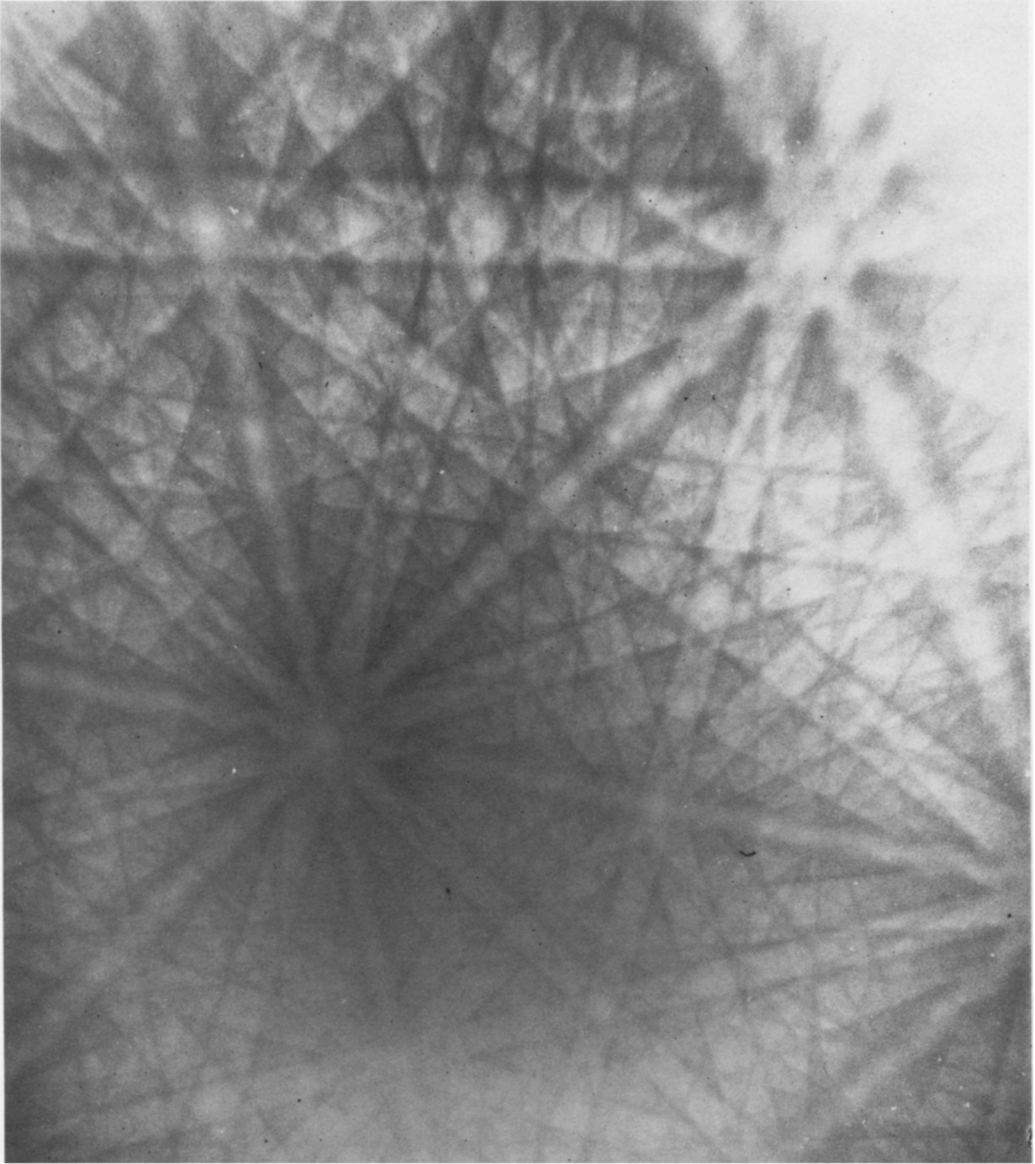


FIG. 8. A back diffraction pattern from one of our particles.

variations in the surface free energy with orientation. Finite facets arise when some of orientations have lower free energies than others. For example, if the (111) face had a low free energy, we would observe a large (111) face. We do observe finite (100) and (111) facets on our particles. However, analysis of Fig. 3d indicates that the (100) and

(111) faces only cover a total of 16% of the particles surface. The bulk of the surface is curved. One can show that the curved regions of the particles are made up of stepped surfaces (16). Thus, it seems that 84% of the surface of our particles is stepped. This implies that at 1200°C, there is not a large difference between the free

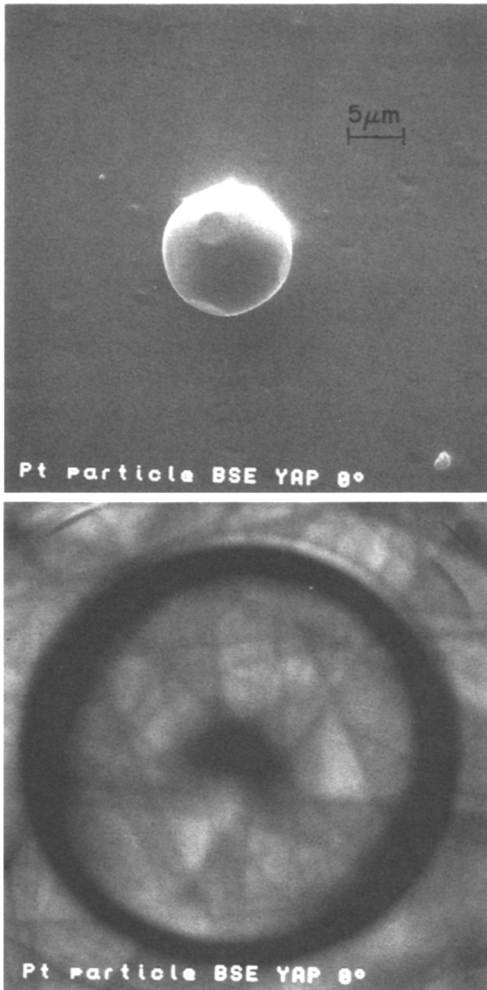


FIG. 9. Top, electron micrographs of platinum on platinum particle. Bottom, channeling pattern taken in the region of particle. The channeling pattern in the center of the photograph comes from the particle. The channeling pattern along the edges of the photo comes from the support.

energy of the (100) and (111) faces, and the free energies of stepped surfaces. Further, the (100) face is larger than the (111). That means that the (100) face has a lower surface free energy than the (111). Analysis of these data indicates that the (100) facets have a surface free energy which is only 3% lower than the surface free energy of the (111) facets and only 4% lower than that of all of the stepped surfaces.

We said "all stepped surfaces" in the last paragraph. However, if we look carefully at the data there is an exception. Note that there is a sharp boundary between the (100) surfaces and the curved regions in Fig. 3d. One can show theoretically (16) that if all step surfaces which are just slightly inclined with respect to the (100) face were stable, we would observe a gradual transition between the (100) faces and the curved regions in Fig. 3d. The fact that we instead observe a sudden change in the angle of inclination at the boundary of the facet implies that some inclinations (i.e., some stepped surfaces) are unstable to formation of hill and valley structures. In fact we observe the hill and valley structures in Fig. 3c. This means that certain stepped surfaces of platinum should be unstable upon heating.

We can use the angle of inclination in Fig. 3d to determine which faces of platinum would be stable toward heating to 1200°C in vacuum or in 10^{-7} Torr of oxygen. Figure 10 shows a plot of the stability boundary determined in this way. From our data we conclude that Pt(111), Pt(110), Pt(210), Pt(211), Pt(410), Pt(611), and stepped surfaces in between should all be stable upon heating to 1200°C. Pt(100) should be stable

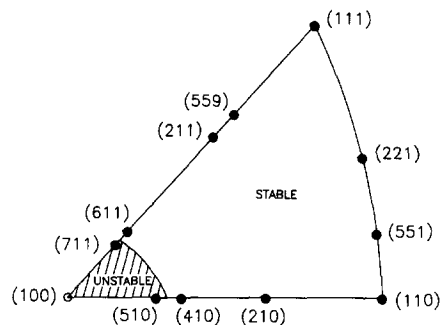


FIG. 10. A plot of the stability of the various planes of platinum as determined from the equilibrium shape measurements in Fig. 3d. The planes which are in the region labeled "stable" did not facet during our experiments. The planes which are in the region labeled "unstable" were found to facet into hill and valley structures upon annealing to 1200°C in 10^{-7} Torr of oxygen. Note: The (100) plane is at the boundary of the unstable region. However, it is stable.

too. However, Pt(510) and Pt(711) should be unstable.

In the previous literature, Blakely and Somorjai (18) examined the stability of several single crystal planes. The data in Fig. 1 generally agree with the observations of Blakely and Somorjai. However, Blakely and Somorjai found that the (559) and (551) faces of platinum facet into hill and valley structures with finite (100), (211), and (221) planes. We do not have any evidence for faceting around the (551) or (559) regions of our sample. We also do not observe formation of finite (211) or (221) planes. Therefore, it appears that the (559) and (551) planes are stable on our samples even though Blakely and Somorjai find that these faces are unstable. At present, we do not have any explanation for this discrepancy.

We also do not understand why after a long anneal, the particles align themselves so that they are in an epitaxial relationship with the support. We deposit particles on a platinum foil which is covered with a thin layer of oxide. The particles start out as drops with no distinct structure. Upon annealing, the particles change to a single crystal with distinct facets. However, we have found that facets initially do not have a particular relationship to the support. Nevertheless, with further annealing the particles were found to slowly rotate so that they are in a near epitaxial relationship with the platinum foil. All of this occurs even though initially there was a thin layer of silica between the particles and the foil. At present, we do not understand the forces which cause the particles to rotate. Therefore, we simply report our observations, and hope that someone else can explain them.

IMPLICATIONS AND SPECULATIONS

Before closing, we did want to discuss some of the significance of our findings. Our most interesting observation is that the equilibrium shape of clean platinum is almost spherical, not cubo-octahedron. The flat facets cover a small fraction of the total surface. Most of the surface is curved which

implies that most of the surface is stepped or kinked (16). We have done all of our measurements on particles larger than $1 \mu\text{m}$. However, at least in our size range, the particle shape is independent of particle size. Such observations are not surprising in light of the recent literature on equilibrium shapes of clean metals (7-17). However, the results do contradict statements which are found in most standard textbooks in catalysis.

Of course, we have measured the equilibrium shape of clean platinum at high temperature. One would not necessarily expect to observe such shapes in actual working catalysts. Our observations imply that the variation in the free energy of platinum with crystal face is small. We cannot calculate an absolute surface free energy from our measurements (we also need a vapor pressure). However, we know that the surface energy only varies by 4% with crystal face. If we assume that the surface free energy of platinum is 2340 erg/cm^2 (19), then we calculate that the surface free energy of platinum only varies by 92 erg/cm^2 with crystal face. By comparison, if we adsorb 1×10^{15} molecules/cm² of a gas with a free energy of adsorption of 10 kcal/mole onto the surface of our particles, the surface free energy will change by 700 erg/cm^2 . It is not unusual to find heats of adsorption which vary by 5 kcal/mole with crystal face, i.e., 350 erg/cm^2 . This means that a small variation in the heat of adsorption of a gas with crystal face will make a significant change in the variation in the surface energy with orientation. Such a variation should produce a change in the equilibrium shape of the platinum. As a result, the equilibrium shape of platinum should change according to which adsorbates are present. Recent publications of Schmidt and co-authors (20) and Shi *et al.* (21) show experimental evidence of this. Further evidence is given in Fig. 6. As a result, the actual particle shapes in a working catalyst may be determined by the species which are present in the reactor and not by the equilibrium shape of clean platinum.

Still, many of the models we have of the influence of particle size upon reactivity are based on the idea that the particles in a catalyst will eventually reach their equilibrium shape. The equilibrium shape is usually assumed to be a cubo-octahedron with flat faces and sharp edges. It is thought that in a large particle only a small fraction of the surface is stepped. Yet, our particles have steps on 84% of their surface! While our sample preparation procedures are far different than those used in conventional catalysts the equilibrium shape of clean platinum is clearly not a cubo-octahedron. Thus, some well-established ideas in catalysis need to be reexamined based on our findings.

CONCLUSIONS

In summary then, we have found that at equilibrium, clean platinum particles have a rounded shape with distinct (100) and (111) facets and curved (i.e., stepped) regions in between. At 1200°C only 16% of the surface of our particles is covered by the facets; the majority of the surface is stepped. Thus, some well established ideas in catalysis need to be reexamined based on our findings.

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