

The Effects of Gas Adsorption on Particle Shapes in Supported Platinum Catalysts

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Previous work has shown that the shapes of the metal particles in a supported platinum catalyst are substantially altered when the catalyst is treated in an appropriate adgas. However, at present it is unclear why the shape changes occur. In the work here, simple first-order calculations were done to examine the effects of hydrogen, nitrogen, and carbon monoxide on the equilibrium crystal shape of the platinum particles in a supported platinum catalyst. The calculations assumed that the main effect of the gaseous environment was to change the surface free energy of the facets on the platinum particles. The results of the calculations showed that when a clean platinum particle is equilibrated in nitrogen, the shape should not change significantly. However, Pt(100) facets should grow in hydrogen while Pt(210) facets should grow in carbon monoxide. By comparison, previous experiments have shown that Pt(100) facets do grow in hydrogen. Little change in shape is observed in nitrogen. Thus, it seems that changes in the surface free energy of the facets in the metal particles on a supported metal catalyst due to the presence of an adgas play an important role in the shape changes which are observed. © 1989 Academic Press, Inc.

INTRODUCTION

Recent work has shown that one can modify particle shapes in supported metal catalysts by exposing the catalysts to an appropriate adgas and waiting for the particle shapes to equilibrate (1, 2). Figure 1 shows some of the changes which were observed. The catalyst shown in the figure was produced by evaporating platinum onto a smooth silica support, annealing in hydrogen or nitrogen for 6 h at 900 K (2), and then rapidly quenching the sample down to room temperature. The catalyst was then transferred into a transmission electron microscope for analysis. Note that, experimentally, all of the particles in the catalyst show cube-like shapes with distinct facets after the catalyst equilibrated in hydrogen. In contrast a rounded shape is seen when the particles are equilibrated in nitrogen. Electron diffraction shows that the facets in the

hydrogen-treated catalysts are Pt(100). Very similar shapes were observed previously by Wang *et al.* (1), which suggests that they are intrinsic to platinum.

It is not clear, at present, why the shapes are as observed in Fig. 1. Wang *et al.* (1) propose that initially the metal particles in the catalyst shown in Fig. 1 are covered with carbon or oxygen. The carbon and oxygen are removed when the catalyst is treated in hydrogen, but it is not removed when the catalyst is treated in nitrogen. As a result Wang *et al.* suggest that Fig. 1 (right) is representative of the equilibrium crystal shape of adsorbate-covered particles, while Fig. 1 (left) represents the equilibrium crystal shape of a clean platinum surface.

In contrast, Shi *et al.* (2) note that the hydrogen could also adsorb on the surface. The adsorption would lower the free energy of certain facets on the particles. As a result those facets would grow in the presence of the adgas. So far, all of the work has been qualitative. It is not known whether the effects described by the models in Refs. (1

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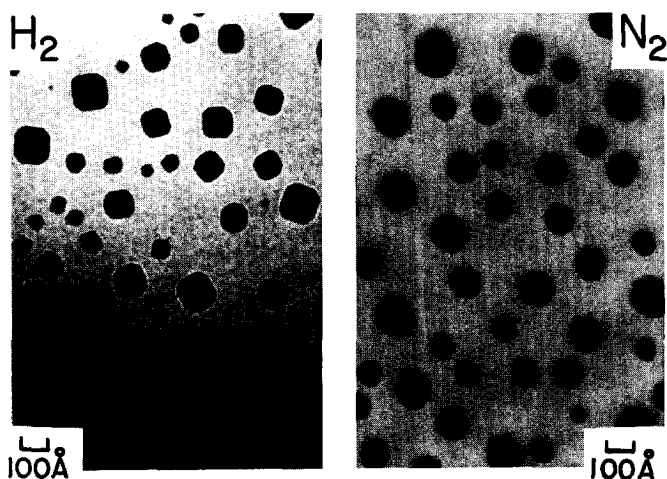


FIG. 1. The particle shapes observed after evaporating platinum onto a smooth silica support and then annealing in hydrogen or nitrogen for 6 h at 900 K. From Ref. (2) with permission.

and 2) are large enough to cause changes in particle shape under the conditions of the previous experiments. The detailed shape changes expected from these models are largely unknown. As a result, it is unclear whether either of these models can be used to explain the experimental data.

In the work here, some simple first-order calculations were done to see if the free energy changes due to the adsorption of the adgas were large enough to have a significant effect on the particle shapes in a supported platinum catalyst. An attempt was also made to calculate the shape changes which should occur under the conditions used for the previous experiments (1, 2). A fairly phenomenological approach was taken in the calculations. Particle shape and thermal grooving data from the literature were used to estimate the surface energy of the facets on a clean platinum particle as a function of orientation. Experimental adsorption/desorption data were then used to estimate the changes in the surface free energy of the facets due to the presence of the adgas. Next, the Wulff (4, 5) construction was used to calculate the changes in particle shape which should occur.

The calculations are not very sophisticated. Further, it is unclear whether the

shapes which are observed experimentally are equilibrium shapes. There is also considerable uncertainty in the data used for the analysis. However, surprisingly good agreement with experimental data was obtained using this simple model.

ANALYSIS

The theory of equilibrium particle shapes was worked out years ago (3-5). Gibbs (3) showed that the equilibrium shape of a small particle is determined by the variation in the surface free energy of the particle with orientation. With a water droplet, for example, there are no variations in the surface free energy with orientation (3). As a result, a water droplet is spherical in the absence of gravity. With a metal, however, some of the arrangements of the surface atoms have a lower free energy than others. As a result, those arrangements grow preferentially (4, 5).

In 1906 Wulff (4) proposed a scheme to calculate the equilibrium shape of a metal particle. Wulff assumed that the surface free energy of a facet on a metal particle was a function of the facet's crystallographic orientation but not of the facet's size. He then showed that one could calculate the shape of a metal particle graphically

from a plot of the surface free energy per unit area versus surface orientation. Wulff's graphical procedure is now called the Wulff construction.

Later work (5) has shown that the Wulff construction is rigorous for a particle which is large enough so that the surface free energy per unit area of the various facets on the particle is not a function of the particle size. However, it gives incorrect shapes for small metal particles ($< \sim 20 \text{ \AA}$) due to edge (finite size) effects (5, 6).

Figure 2 illustrates how the particle shape of a metal particle might vary with temperature (5, 6). At absolute zero, the equilibrium shape is a polyhedron. Figure 2 shows a particle with distinct (111), (110), and (100) facets and sharp edges. Such a shape is characteristic of many metals at 0 K. Figure 2 also illustrates how the particle shape changes with temperature. As the temperature rises, the edges between the particles start to be rounded. The rounded regions are called rough regions and are thought to be highly disordered. The rough regions expand with increasing temperature. Eventually, the crystal shape is a sphere.

The diagrams in Fig. 2 show sharp boundaries between the facets and the rough regions. This is an artifact due to limitations on our computer graphics routine.

Winterbottom (7) considered the effect of the support on the equilibrium crystal shape. He showed that in the limit of a flat support, the equilibrium crystal shape was a truncated form of the equilibrium shape of an isolated particle, as illustrated in Fig. 3. Winterbottom's arguments can be directly applied to the metal particles in a supported metal catalyst. As a result, one can use the Wulff construction to calculate the shape of the particles in a catalyst, provided that the support is flat on the length scale of the particle and that the particles are large enough for the thermodynamic limit to apply.

One can imagine how gas adsorption might change the equilibrium shape of the

metal particles in the catalyst. Gas adsorption will lower the free energy of all of the faces on a metal particle. However, since the heat of adsorption varies with crystal face, some faces will be affected more than others. Qualitatively, those faces which bind the adgas strongly will be stabilized at the expense of faces which bind the adgas less strongly. As a result, at equilibrium, the faces which bind the adgas most strongly might tend to grow preferentially.

One can put this effect on a more quantitative basis using some ideas proposed by Gjostein (8) and Herring (12). Earlier work by Herring (5) had shown that if one knows the equilibrium crystal shape of a clean metal particle, one can back-calculate the variation in the free energy with orientation. Winterbottom and Gjostein (9) describe the procedure in more detail. Gjostein noted that when gas adsorbs on a metal particle which is large enough for thermodynamics to apply, the free energy of the facets on the particle changes according to

$$\Delta G = - \int_{-\infty}^{\mu} \theta d\mu, \quad (1)$$

where

ΔG = the change in the surface free energy per unit area of the facet = the free energy of adsorption per unit area

θ = the coverage in molecules per square centimeter

μ = the chemical potential of the gas over the substrate.

For an ideal gas

$$\mu = RT \ln(P) + \mu_0. \quad (2)$$

Hence, if the free energy of the various faces of the metal is known from the clean particle shape and θ is known as a function of pressure and orientation, one can calculate how the free energy of each of the faces on the metal particles will change in the presence of an adgas. One can then use the Wulff construction (4, 5) to calculate how the equilibrium particle shape should

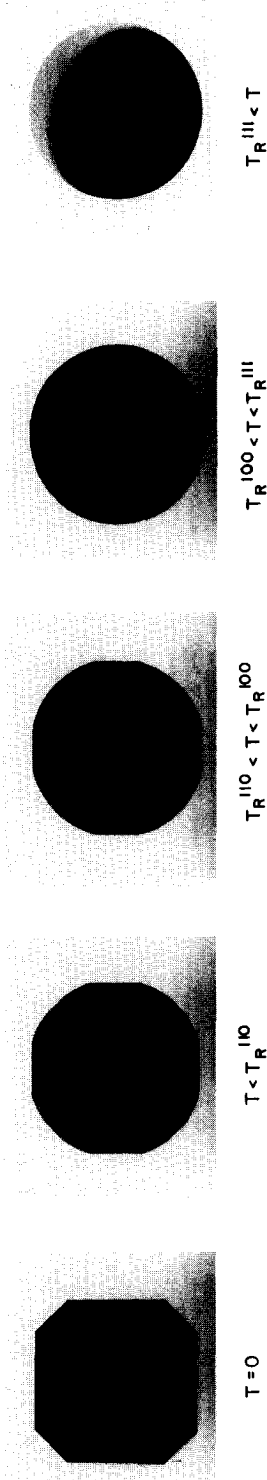


Fig. 2. A qualitative picture of the evolution of the equilibrium particle shape with temperature. T_r indicates the roughening temperatures for the various facets.

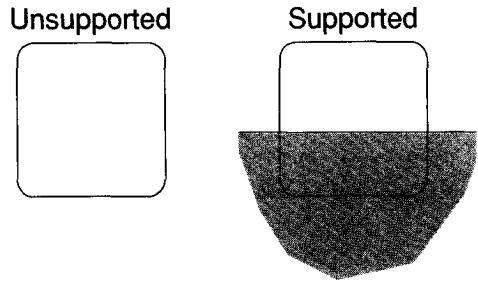


Fig. 3. A schematic showing the effects of the support on the equilibrium crystal shape, after Winterbottom (7).

change due to the presence of the adgas, assuming that the particle is large enough that the thermodynamic limit applies.

Surprisingly, however, few calculations of this type have appeared in the literature. Gjostein's work was qualitative. Sharmon and Robertson (10, 11) tried to apply Gjostein's formalism to predict particle shape changes. However, they did not have the data they needed to do the calculations. Herring (12) also did some qualitative calculations on the effects of adsorption of the particle shapes. However, he did not have the data he needed to quantify them. Much more recently Shi (13) used a pairwise additive potential to estimate θ as a function of μ . He then calculated the influence of gas adsorption on the equilibrium shape at 0 K from the Wulff construction. Kariotis *et al.* (14) examined the effect of gas adsorption on the roughening transition. However, all of this work was done in a fairly general way. At present there has not been any published attempt to apply these methods to a real system to see if the effects are important.

The objective of the work here was to see how the equilibrium shapes of the particles in a supported platinum catalyst should change due to the presence of CO, N₂, and H₂. The calculations were rather straightforward. The starting point for the calculations was Heyraud and Metois's measurements of the surface energy as a function of orientation for a series of clean gold parti-

cles at 1000 K (15, 16). Thermal grooving data for the relative surface energy anisotropy of platinum (17) and gold (9) were then used to estimate the surface energy of a clean platinum particle as a function of orientation at 900 K.

Next, Eq. 1 was used to estimate the change in the surface free energy as a function of orientation. It was assumed that the adsorption followed a multistate Langmuir adsorption model, where the total coverage of the adgas, θ , is given by a sum of coverages in a series of individual adsorbed states, θ_m :

$$\theta = \sum_m \theta_m, \quad (3)$$

with

$$\frac{d\theta_m}{dt} = s \left(\frac{Pv_a}{4RT} \right) (1 - \theta_m/\theta_{0,m})^n - k_d(\theta_m/\theta_{0,m})^n, \quad (4)$$

where

θ_m = the coverage of the adsorbate in the m th adsorbed state in molecules per square centimeter

P = the partial pressure of the adsorbate

s = the sticking probability of the adsorbate

v_a = the molecular velocity of the adsorbate in the gas phase

$\theta_{0,m}$ = the saturation coverage of the adsorbate in the m th state

k_d = the rate constant for desorption of the adsorbate

R = Boltzman's constant

T = temperature

n = the order of the adsorption/desorption process

At equilibrium $d\theta_m/dt = 0$. Combining Eqs. 1, 2, 3, and 4 yields

ΔG

$$= \sum_m \left[-n \theta_{0,m} RT \ln \left\{ 1 + \left(\frac{Pv_a s}{4 k_d RT} \right)^{1/n} \right\} \right]. \quad (5)$$

The implication of Eq. 5 is that if one knows s , k_d , and n as a function of pressure on all of the faces of a crystal at some temperature then one can calculate the change in the free energy of the various facets on that crystal due to adsorption of gas at that temperature. The change in particle shape can then be calculated via the Wulff construction (4, 5). In fact, s , k_d , and n are not known at the conditions where changes in the shapes of small platinum particles were observed previously (~ 900 K and 1 atm). However, there is data for s , k_d , and n near room temperature in UHV for several faces in the stereographic triangle. One can obtain estimates of the parameters in Eq. 4 from the UHV data.

In the calculations here it was assumed that the sticking probability and activation energy of desorption were independent of temperature. Variations in the heat of adsorption with coverage were ignored. If no adsorption data was available on a given face, coverages on that face were estimated using a multiple site model (e.g., Pt(411) was assumed to have a mixture of (100) and (211) sites). Clearly, this is an approximation. However, since this is the first published calculation of this type, a simple approach seemed to be an appropriate place to start.

RESULTS: CLEAN PLATINUM

Figure 4A shows the shape calculated for a clean platinum particle at 900 K. One observes distinct (100) and (111) facets and a series of rough regions. The figure also shows sharp boundaries due to an artifact in our computer plotting procedure.

The shape in Fig. 4A follows closely the shape observed previously for a "clean" gold particle (16). Gold and platinum, of course, are different. However, thermal grooving data indicates that the relative surface energy anisotropy of platinum (17) and gold (9) are almost the same. Thus, from the Wulff construction a clean platinum particle should look very similar to a clean gold particle.

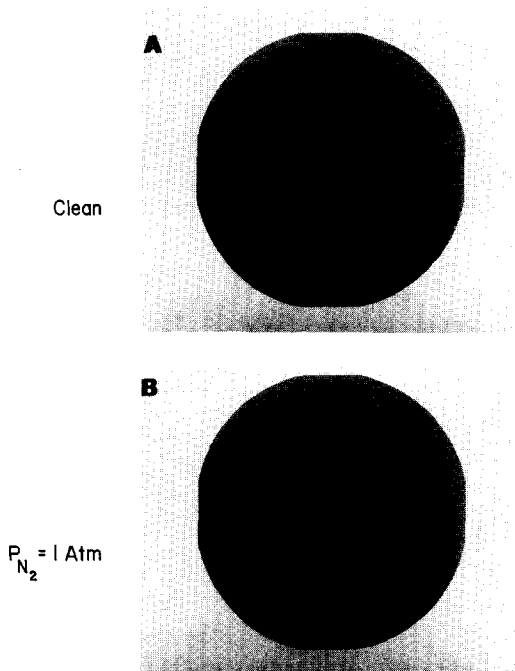


FIG. 4. The effect of N_2 on the calculated equilibrium crystal shape of a platinum particle.

If one uses the thermal grooving data to scale the Metois's (15) data for the surface energy of gold to platinum, then one calculates that the surface energies of the (111), (100), and rough regions are 2264, 2281, and 2340 erg/cm², respectively. As a result, it seems that the surface (free) energies of the various faces of platinum only vary by about 76 ergs/cm² with orientation. By comparison, if 1×10^{15} molecules/cm² of a gas with a free energy of adsorption of 10 kcal/mole adsorbed, the free energy of the system would change by about 700 erg/cm². This is a large change compared to the difference in the surface energy of the various faces of platinum. Hence, a small change in the free energy of adsorption with crystal face could make a substantial change in the equilibrium particle shape.

RESULTS: NITROGEN

Of course, if the free energy of adsorption is independent of crystal face, even if the free energy of adsorption is large, no

shape change will occur. For example, consider nitrogen. Wilff and Dawson (18), and Schwaha and Bechtold (19) examined the adsorption of nitrogen on several faces of platinum. They found that the sticking probability of nitrogen is small. Further, the sticking probability and activation energy of desorption of nitrogen do not vary significantly with crystal face. As a result, ΔG calculated from Eq. 4 is almost independent of crystal face.

Figure 4B shows how the equilibrium shape of a platinum particle should change when it is exposed to 1 atm of nitrogen at 900 K. Note that the shape calculated for a nitrogen-covered particle is essentially indistinguishable from that of a clean platinum particle. According to the calculations, one does get a reasonable nitrogen coverage (~ 0.1 monolayers) at higher pressures. However, little difference among the various faces is seen. As a result, exposure to nitrogen should not produce a significant change in the equilibrium shape of the particles in a supported platinum catalyst.

RESULTS: HYDROGEN

The situation is entirely different with hydrogen. According to McCabe and Schmidt (20), the activation energy of desorption of hydrogen varies significantly with crystal face. Pt(100) binds hydrogen most strongly, while Pt(110) and Pt(111) binds hydrogen most weakly. An intermediate binding energy is seen on Pt(210) and Pt(211). There also are changes in the sticking probability with crystal face. However, the effects of variations in the sticking probability are small compared to the effects of changes in binding energy.

If one substitutes the kinetic data in Ref. (20) into Eq. (4), one finds that at 900 K the hydrogen coverage on all of the faces of platinum should be negligible at pressures below 5×10^{-4} Torr. However, at higher pressures the various faces begin to adsorb gas. Pt(100) fills up first. Pt(211), Pt(210), and the rough regions fill up next. The Pt(111) face fills up last. Since the Pt(100)

face fills up first, the free energy of the Pt(100) face will be lowered (i.e., the Pt(100) face will be stabilized) in the presence of hydrogen.

Figure 5 shows how this stabilization should change the equilibrium crystal shape of the platinum particles in a supported platinum catalyst. The Pt(100) faces which are stabilized in hydrogen are predicted to grow when the catalyst is exposed to hydrogen. Simultaneously, the Pt(111) faces are expected to shrink. With 1 atm of hydrogen, the calculations suggest that the

shape should be a rounded cube at 900 K, as indicated in Fig. 5C.

At present, we do not have a good way to estimate the extent of rounding. While Eq. 5 applies to the rounded (rough) regions of the metal particles, the heat of adsorption on a roughened surface may well be different from the heat of adsorption on a pristine single-crystal plane. As a result, it is difficult to estimate the parameters needed to apply Eq. 5 to the rounded regions of the metal particles.

Theoretically, the rounding is dependent

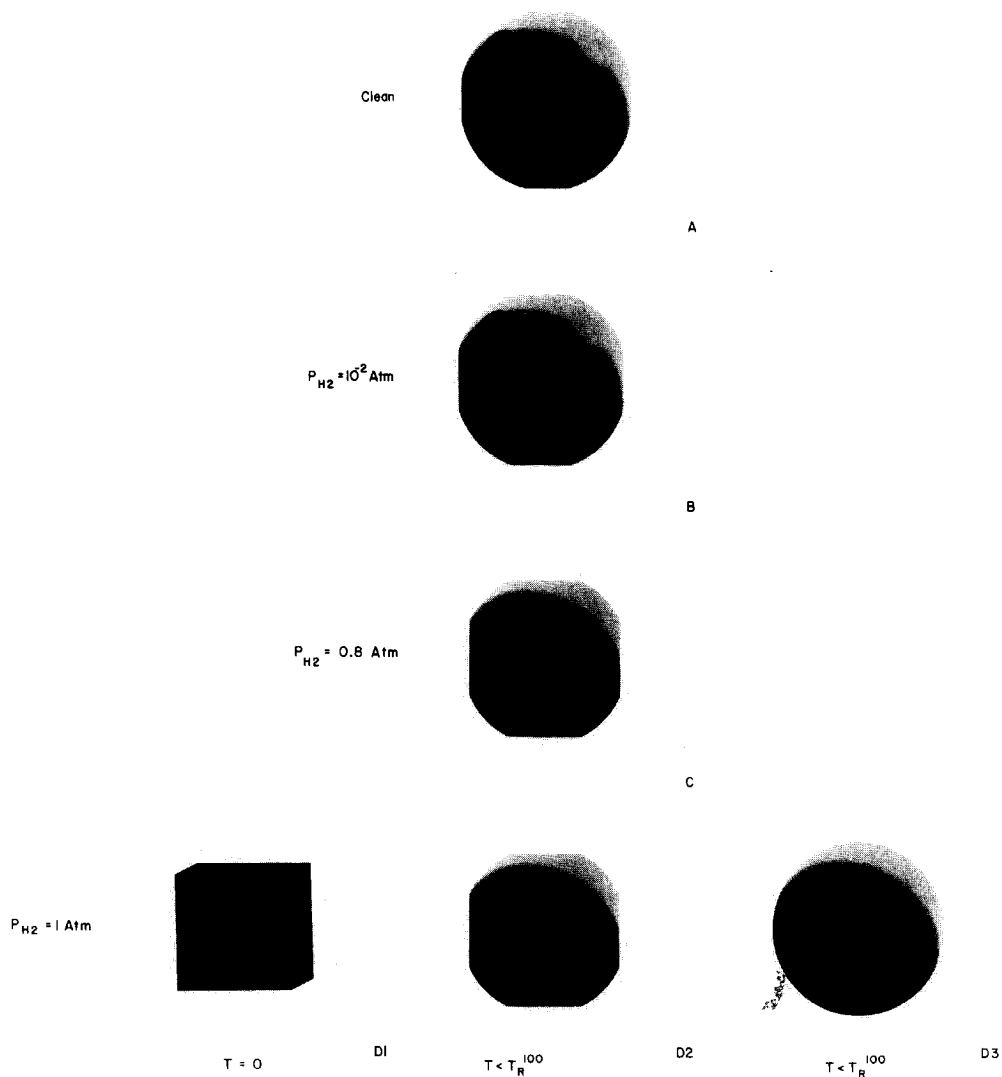


FIG. 5. The effect of H_2 on the calculated equilibrium crystal shape of a platinum particle.

on the temperature, pressure, and a series of parameters called roughening temperatures. T_R^{ijk} . If the actual temperature is greater than the roughening temperature for all of the facets in the particle, then the particle should be a sphere. If instead the temperature approaches zero, the particle shape should approach a polygon. Experimental data can give an estimate of the roughening temperature for a clean platinum particle. One can estimate the degree of rounding of clean platinum from that data. However, it is unclear what happens in hydrogen. If there is no change in the roughening temperature due to the adsorbed hydrogen, then the degree of rounding should not change significantly from that in a clean platinum particle. In such a case, the particle shape at 900 K should be as given in Fig. 5D2. However, Kariotis *et al.* (14) found that the roughening temperature could change due to the presence of an adgas. In Kariotis's calculations, the roughening temperature decreased in the presence of an adgas. If the roughening temperature decreased, the rounded areas in Fig. 5D2 would increase. Hence, the shape might approach that of a sphere. If instead the roughening temperature would increase, the crystal shape should approach a cube.

Of course, if one wanted to make a specific shape, one could always compensate for the changes in roughening temperature by changing the equilibration temperature. Theoretically, the shape of a hydrogen-covered particle should approach a cube in the zero-temperature limit and a sphere in the high-temperature limit. From a practical standpoint, one would not go to too low of a temperature because the equilibration time would become too long. However, in principle, one should be able to produce any particle shape between that in Fig. 5D1 and 5D3, if one were willing to wait long enough for the system to come to equilibrium. Hence, according to the calculations here, one should be able to get (100) facets to

grow in a supported platinum catalyst by treating the catalyst in hydrogen.

RESULTS: CARBON MONOXIDE

Large shape changes are also expected if the platinum catalyst is treated under 1 atm of carbon monoxide. McCabe and Schmidt (21) examined the adsorption of carbon monoxide on several faces of platinum. They found that CO is bound most strongly on Pt(210) and least strongly on Pt(110) and Pt(111). There are also some significant variations in the sticking probability of CO on the various faces of platinum. Other work shows that various stepped surfaces also bind CO strongly.

If we substitute the kinetic data in Ref. (21) into Eq. (3), we predict that the CO coverage on all of the faces of platinum should be negligible at 900 K at pressures below 1×10^{-5} Torr. However, at higher pressures the various faces begin to adsorb gas. According to the calculations, the rough regions should start to fill up first. As a result, initially, the rough regions should grow, as illustrated in Fig. 6B.

At higher pressures, the fact that the Pt(210) face binds CO most easily starts to play an important role in the calculations. There is no Pt(210) facet on a clean platinum particle. Instead Pt(210) lies in the rough regions. However, according to the calculations here, the Pt(210) face is stabilized in the presence of the CO. As a result, the Pt(210) face could appear at higher CO pressures. The crystal shape would approach that illustrated in Fig. 6C1 to 6C3. Further increases in the CO pressure should cause the Pt(210) face to grow substantially, as illustrated in Fig. 6D1 to 6D3.

From the work here, it is difficult to predict whether the Pt(210) face will be rounded or flat. If the Pt(210) facet is below its roughening temperature, then one would expect a flat face such as that in Fig. 6C2 and 6D2. Alternatively, if the Pt(210) facet is above its roughening temperature, the particle shape might look like that in Fig.

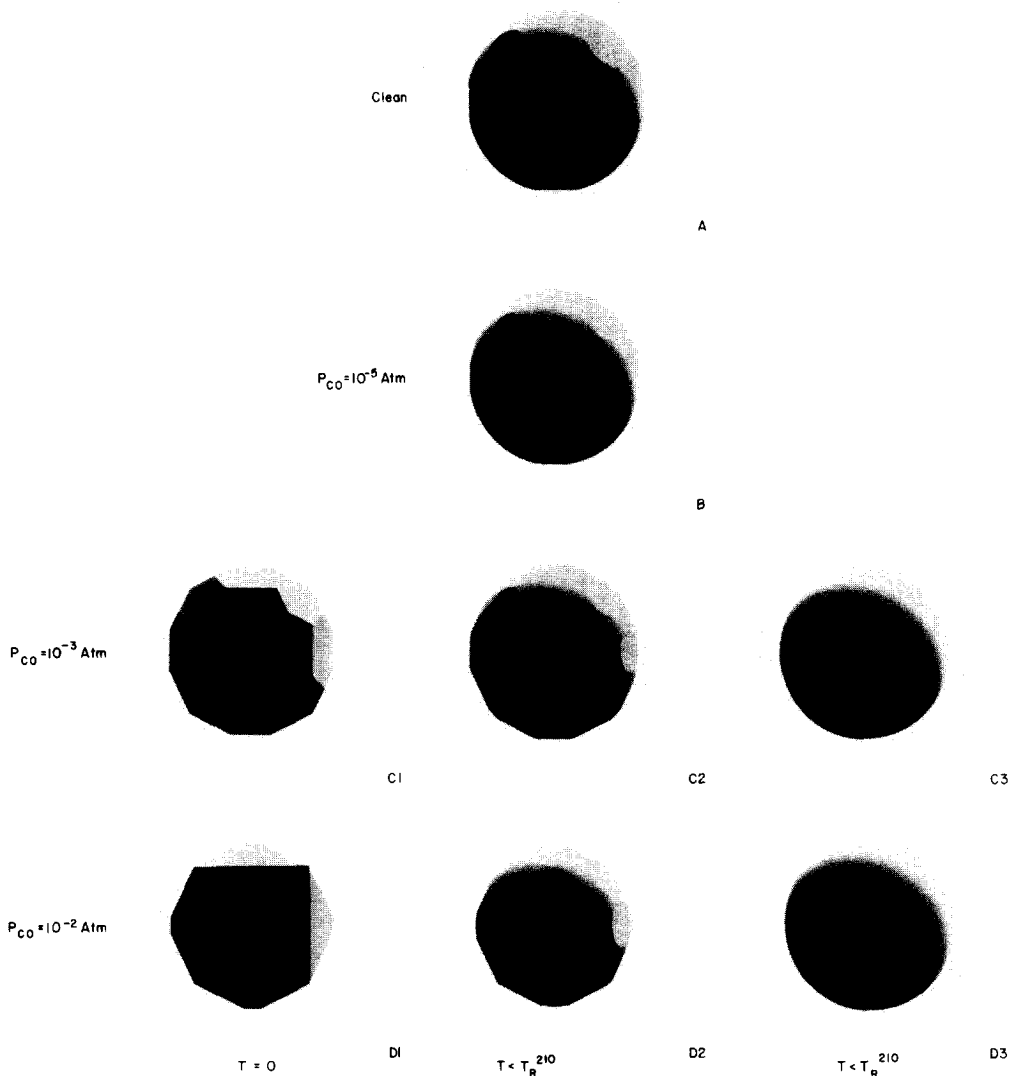


FIG. 6. The effect of CO gas on the calculated equilibrium crystal shape of a platinum particle.

6C3 and 6D3. Alternatively, in the zero-temperature limit, the particle shape might even approach the polygon shown in Fig. 6C1 and 6D1. It is difficult to predict, from first principles, which of these possibilities will be seen. However, we note that experimentally, Pt(210) is one of the more stable faces in the stereographic triangle. It does not reconstruct after treatment at high temperatures in a variety of atmospheres (22).

It shows clear LEED patterns at 1000 K. Thus, the roughening temperature of Pt(210) is probably well above 900 K. Hence, the most likely possibility is that the platinum particles would look like those in Fig. 6C2 and 6D2 at 900 K.

DISCUSSION

Clearly, the results above show that the changes in the surface energy due to gas

adsorption should produce large changes in the shapes of the particles in a supported platinum catalyst. The calculations suggest that some facets should grow, while others should shrink. There also is the possibility of a facet which does not exist on a clean particle appearing in the presence of an adsorbate. Thus, the calculations suggest that it should be possible to substantially alter the shapes of the particles in a supported platinum catalyst by exposing the catalyst to an appropriate adgas.

Of course, these are calculations. Several assumptions were made about the nature of the adsorption. Hence, it is unclear whether the calculations are accurately reflecting nature. Therefore, it is useful to try to compare the results of the calculations in Figs. 4 and 5 to experimental data in Fig. 1.

Note there is a close correspondence between the shapes predicted by the model here and the shapes observed experimentally. The calculations suggested that square particles with distinct (100) facets should be seen in hydrogen. They are observed. In contrast, the calculations suggested that rounded particles should be seen in nitrogen. Again the predicted shapes are observed. There even seems to be some correspondence between the detailed shapes in the calculations and in the experiments. Thus, it appears that the calculations are in close agreement with the experiment.

Admittedly, the apparent agreement between the detailed shapes in Fig. 1, and those in Figs. 4 and 5, is probably exaggerated. Experimentally, it has been found that there is some variation in the particle shape from run to run. For example, square-shaped particles were observed whenever the catalyst was treated in hydrogen. However, sometimes the particles seemed to have sharp corners. Other times, the corners were highly rounded. The details of the quenching procedure seem to play an important role in determining the observed crystal shape. The particles shown are typical ones that were observed.

The typical shapes agree quite well with the calculations. However, there has been some run-to-run variation in the data. There also is the problem that the shapes have been found to be quite different in the areas of the support which are not flat on the length scale of the particles (2). As a result, a more detailed comparison between calculation and experiment does not seem productive at the present time.

Still, the results here show clearly that the changes in the surface free energy in the presence of an adgas are sufficient to produce major changes in the particle shapes in a supported metal catalyst. Further, there appears to be a close correspondence between the calculated shape changes and those observed experimentally. As a result, it seems that the model of Shi *et al.* (2) is a reasonable representation of the data.

Nevertheless, at this point there is still more work to do before we can conclude that the particle shape changes in Fig. 1 are due to the adsorption of adgases. The starting point for the calculations was thermal grooving measurements of the surface energy anisotropy of clean platinum from Ref. (17). However, the data in Ref. (17) were not taken under pristine conditions. If for example the surface energy of the Pt(100) face was actually considerably lower than that of a Pt(111) face, rather than higher than the (111) face as reported in Ref. (17), one would reach much different conclusions about the interpretation of the data in Fig. 1. The calculations also assumed that the adsorption/desorption data of McCabe and Schmidt could be simply extrapolated to high pressures and temperatures. While the details of this extrapolation are certainly subject to question, the key feature of the calculation is that those planes which bind the adgas most strongly grow at the expense of those planes which bind the adgas less strongly. We have found that the qualitative shape is not strongly affected by the exact numerical value of the parameters, only by the ordering of the binding energies, provided the pressure is

high enough to get a sufficient coverage of adgas. The calculations here suggest that if one gets coverages in the order of 10% of a monolayer, one could make significant changes in the crystal shape. However, without additional measurements, one does not know whether this condition is satisfied under the conditions used to take the data in Fig. 1. Thus, there is still much uncertainty in the interpretation of the data in Fig. 1, even though the calculations here do reproduce them.

CONCLUSION

Still, the results here show clearly that the changes in the surface free energy in the presence of an adgas are sufficient to produce major changes in the particle shapes in a supported metal catalyst. Further, there appears to be a close correspondence between the calculated shape changes and those observed experimentally. No claim is made that the calculations done here are particularly sophisticated. Data were used to estimate everything. However, surprisingly good agreement with experiment was obtained with this simple model. As a result, it seems that changes in the surface free energy in the presence of adgasses play an important role in determining the shape changes which occur.

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