

# Intraparticle Redispersion of Rh and Pt-Rh Particles on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> by Oxidation-Reduction Cycling<sup>1</sup>

T. WANG AND L. D. SCHMIDT

*Department of Chemical Engineering and Materials Science, University of Minnesota,  
Minneapolis, Minnesota 55455*

Received December 9, 1980; received March 9, 1981

Morphologies produced by oxidation and reduction of 20- to 200-Å diameter Rh and Pt-Rh alloy particles on planar amorphous SiO<sub>2</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are examined using high-resolution scanning transmission electron microscopy. Specimens are prepared by vacuum deposition of metals onto thin oxide supports which are then heated in air or H<sub>2</sub> at pressures of 1 atm. It is found that redispersion of small crystallites of Rh can be achieved by first oxidizing Rh to Rh<sub>2</sub>O<sub>3</sub> in air at ~600°C, and then reducing the oxide particles at lower temperatures. Particles after reduction are converted to small clusters of metal 10-20 Å in diameter or form cracks. Morphologies on Al<sub>2</sub>O<sub>3</sub> substrates are similar. For Pt-Rh alloys, Rh<sub>2</sub>O<sub>3</sub> forms at the edge of Pt metal cores. Reduction at 25°C then produces small Rh particles at the edges of the original particle. Upon heating to 500°C, particles coalesce into roughly their original morphologies, but the cores are primarily Pt and surfaces of particles are enriched in Rh. It is estimated that surface area increases of ~100% may occur by these processes. Two mechanisms are suggested for intraparticle redispersion, one caused by the different interfacial energies of metal and metal oxide on the support and the other arising from the mechanism of oxide formation on a metal surface with a small radius.

## INTRODUCTION

Supported platinum metal catalysts, particularly in hydrocarbon reforming processes, are subjected periodically to regeneration cycles in which they are treated in air at high temperatures and then H<sub>2</sub> in order to remove carbon contamination and redispense the catalyst. Redispersion, the increase of metal surface area, is thought to proceed mainly through volatilization of metals as oxide, chloride, or oxychloride and their redeposition as smaller particles at other locations on the porous oxide support.

However, it has been suggested that redispersion by processes on the surface may also occur, and several mechanisms for this have been proposed. The first involves formation of a metal oxide (1-6), which, because of its stronger interac-

tions with the support (usually  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), spreads over its surface. A second mechanism proposes that during oxidation particles actually split into smaller particles (7, 8), although the observations of this effect and its cause for Pt on Al<sub>2</sub>O<sub>3</sub> have been questioned (5). A third mechanism involves strong metal-support interactions (SMSI) which, as with particle oxidation, produces a large surface area through spreading of particles. The prototype systems exhibiting this effect have been Pt metals on TiO<sub>2</sub> (9). None of the experiments have yielded unequivocal evidence for redispersion, especially as produced by oxidation-reduction cycles.

These processes are difficult to characterize even under laboratory conditions, and under the conditions of oxidation-reduction cycles of industrial catalysts the situation becomes considerably more complicated.

We report here the effects of oxidation-reduction treatment of Rh and Pt-Rh par-

<sup>1</sup> This work partially supported by the Petroleum Research Fund through Grant 10864-AC7.

ticles on amorphous  $\text{SiO}_2$  and on  $\gamma\text{-Al}_2\text{O}_3$ . We show, using electron microscopy, that reduction of  $\text{Rh}_2\text{O}_3$  results in breakup into clusters of smaller metal particles. We believe that this is the first direct evidence for intraparticle redispersion processes. The process can be described as occurring upon reduction of a thin metal oxide particle whose formation should occur during oxidation even in the absence of strong support in interactions.

This work is a continuation of previous studies in this laboratory on Pt, Pt-Pd, Pt-Rh, and Ir on planar amorphous  $\text{SiO}_2$  (10-13). For Pt-Pd the PdO particles grew at the edge of the parent alloy particle. Reduction in  $\text{H}_2$  occurred at room temperature to yield separated Pt and Pd particles with little morphology change except for a contraction of the PdO upon reduction. Reduction of  $\text{Rh}_2\text{O}_3$  from Rh and Pt-Rh particles was not examined in the previous work (12) with that system. Ir reduction (13) exhibited no cracking as reported here, but in final stages of oxidation, tiny (10 Å) particles of Ir metal were left in the oxide.

#### EXPERIMENTAL

Apparatus and procedures have been described in detail previously (10-13). Particles of Rh or Pt-Rh were prepared by vacuum deposition of 10- to 20-Å films of metal onto planar amorphous  $\text{SiO}_2$  or crystalline  $\gamma\text{-Al}_2\text{O}_3$  substrates with thicknesses of 500 Å and heating in a hydrogen atmosphere to form metal particles with diameters of 10 to 200 Å. These were then examined following heat treatment in air or  $\text{H}_2$  using a JEOL JEM 100CX scanning transmission electron microscope.

The thin  $\text{SiO}_2$  substrates were prepared by vacuum-depositing a film of silicon onto rocksalt, dissolving the salt in water, and transferring the Si flake into a silicon disk with a 1-mm diameter hole at its center. The substrates were then trans-

ferred to a quartz tube furnace, heated to 1100°C for 1 hr in air in order to oxidize the entire flake and a 1000-Å thick layer of the disk to amorphous  $\text{SiO}_2$ .

Preparation of  $\gamma\text{-Al}_2\text{O}_3$  substrates was by the anodic oxidation of Al foils developed by Young (14) and described by Ruckenstein *et al.* (4, 7). After anodization of a pure Al foil in a buffered tartaric acid solution, the oxide films were then released by dissolving the metal in a dilute mercuric chloride solution and picking up flakes of  $\text{Al}_2\text{O}_3$  on a gold electron microscope grid. After heating in air at 800°C for several days, the oxide film was completely transformed to crystalline  $\gamma\text{-Al}_2\text{O}_3$  as shown by electron diffraction.

Metal films were vacuum deposited sequentially to a thickness of 10 to 20 Å. The composition of alloy particles was obtained by measuring the weight loss of each metal during the deposition and from quantitative analysis of its X-ray photoelectron spectrum. The alloy compositions determined by these two measurements agreed to within 5%.

Specimens were heated in flowing  $\text{H}_2$  or air at flow velocities of  $\sim 0.1$  cm/sec in a quartz tube furnace. The same region of a specimen was examined repeatedly in an oxidation-reduction sequence. Sequences were obtained for a total of 12 samples of pure Rh on either  $\text{SiO}_2$  or  $\gamma\text{-Al}_2\text{O}_3$  and four samples of Pt-Rh on  $\text{SiO}_2$ . The micrographs of all of these specimens showed consistent results. Rhodium and Pt-Rh alloy supported on amorphous  $\text{SiO}_2$  samples were also examined by X-ray photoelectron spectroscopy as will be described in detail in a later publication. No evidence of contamination was detected since the spectra showed only Pt, Rh, O, Si, and traces of C.

It should be noted that redispersion of metals on the substrate by vapor phase transport of volatile metals or oxides is highly unlikely in these experiments since any gaseous species generated should

have a high probability of removal in the flowing gas.

## RESULTS

### *Rh on Amorphous SiO<sub>2</sub>*

Figures 1a to c show micrographs of a specimen with a 20-Å initial loading of pure Rh on amorphous SiO<sub>2</sub> after heating successively in flowing H<sub>2</sub> at 600°C and then in air at 500 and 600°C, each for 1 hr. At 500°C in air, the diffraction pattern indicates that most of the Rh is oxidized to Rh<sub>2</sub>O<sub>3</sub>, leaving only a small amount of higher contrast unoxidized metal at the core of most oxide particles. After heating to 600°C, all metal diffraction lines have disappeared, and the oxide particles are observed to spread on the substrate. These results are identical to those described previously for oxidation of Rh on SiO<sub>2</sub> (12).

Figures 1d to j show micrographs of the same region following exposures to H<sub>2</sub> for 1 hr at successively increasing temperatures. At room temperature, Fig. 1d, no significant change in morphology or electron diffraction pattern was observed. However, after heating to 150°C (Fig. 1e), a dramatic change in morphology takes place. The oxide particles split into many small clusters which are separated by channels or cracks 5–10 Å wide. Electron diffraction at this temperature showed a weak diffuse fcc pattern, indicating that these small clusters are mostly reduced but not well crystallized. This splitting phenomena seems to occur generally for particles of all sizes between 20 and 200 Å.

Comparison of this micrograph with Fig. 1a shows that each original particle breaks into a cluster of much smaller particles. The geometries of these clusters appear irregular, and most are only 5 to 20 Å in diameter.

The gaps between newly formed crystallites disappear as temperature is increased. By 250°C, Fig. 1f, most channels

were completely filled in by Rh metal, although some large cracks are still evident. The electron diffraction pattern at this temperature showed only the sharp rings of fcc metal.

Subsequent heating of this specimen to higher temperatures in H<sub>2</sub> produces sintering and coalescence of Rh crystallites. Figures 1g to 1j show micrographs of the same region at 350, 450, 550, and 700°C, respectively. Coalescence occurs by growth of larger particles which finally merge with nearby particles. No particle motions greater than a fraction of particle diameter were observed, confirming that atomic migration is the sole mechanism of the sintering in either oxidizing or reducing atmospheres (10–13).

### *Rh on $\gamma$ -Al<sub>2</sub>O<sub>3</sub>*

Alumina substrates exhibit more surface inhomogeneity than do amorphous SiO<sub>2</sub> substrates because they are largely crystalline. Figures 2a to f show a specimen with Rh crystallites supported on Al<sub>2</sub>O<sub>3</sub> after various treatments. Since the substrate had been heated at 800°C for several days prior to metal deposition, no change in substrate morphology at lower temperatures should occur. Neither reduction of Al<sub>2</sub>O<sub>3</sub> or formation of Al-Rh complexes in either atmosphere was detected from the electron diffraction patterns.

The behavior of Rh on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is qualitatively similar to that on SiO<sub>2</sub>. Oxidation of Rh on Al<sub>2</sub>O<sub>3</sub> at 500 and 600°C in air also produced Rh<sub>2</sub>O<sub>3</sub> whose spreading along the substrate takes place at comparable temperatures, although Fig. 2b indicates only partial oxidation of Rh metal. Splitting of the crystallites is observed after heating the specimen in H<sub>2</sub> at 150°C for 1 hr (Fig. 2d). Sintering and coalescence are also similar to those observed on SiO<sub>2</sub>.

It is interesting to note that Rh crystallites are located preferentially at boundaries of Al<sub>2</sub>O<sub>3</sub> grains which are indicated

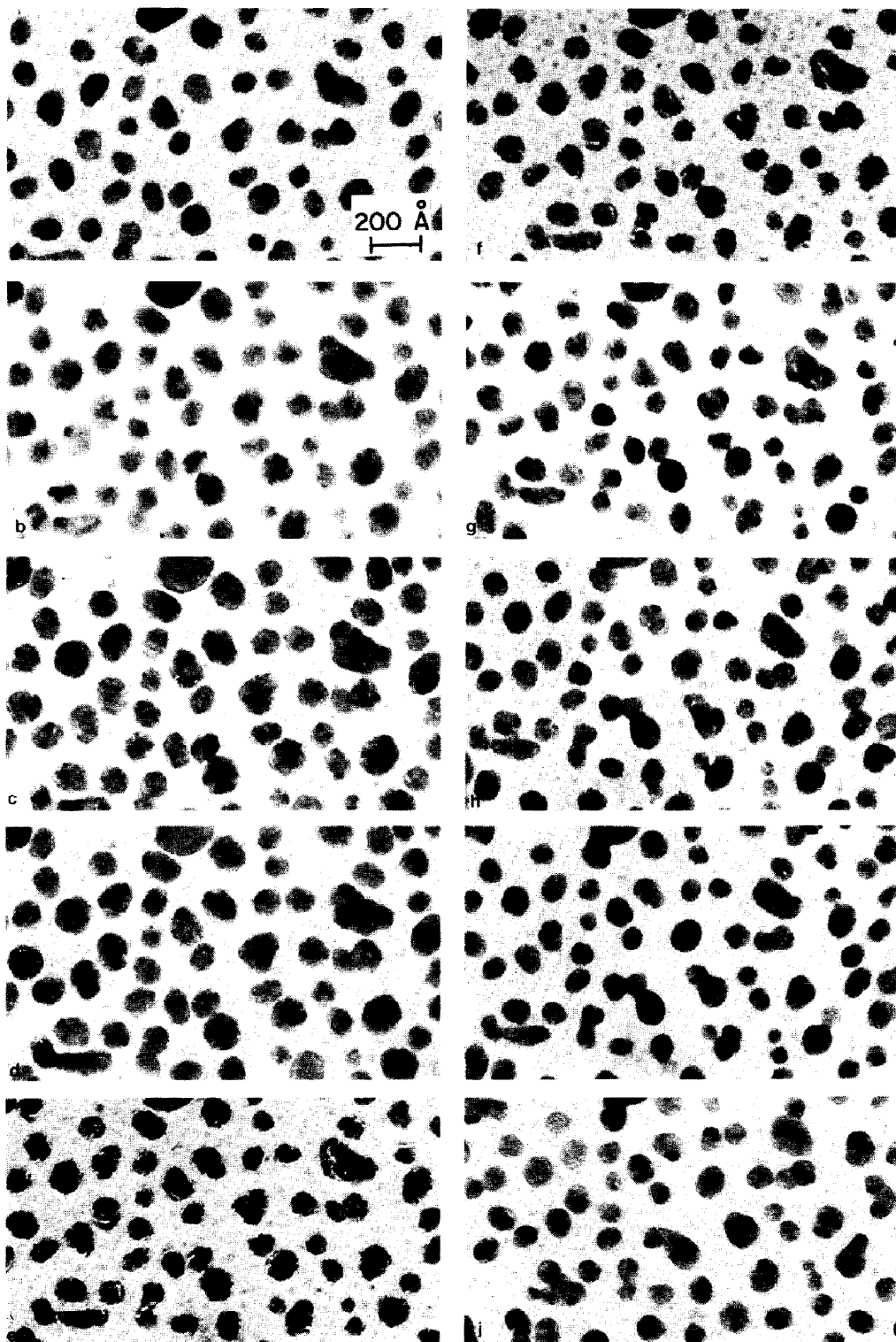


FIG. 1. Transmission electron micrographs showing the morphologies of metal and oxide particles formed by heating pure Rh on  $\text{SiO}_2$  for 1 hr in (a)  $\text{H}_2$  at  $600^\circ\text{C}$ , (b) air at  $500^\circ\text{C}$  and (c) air at  $600^\circ\text{C}$ . This was followed by heating in  $\text{H}_2$  at (d) room temperature, (e)  $150^\circ\text{C}$ , (f)  $250^\circ\text{C}$ , (g)  $350^\circ\text{C}$ , (h)  $450^\circ\text{C}$ , (i)  $550^\circ\text{C}$ , and (j)  $700^\circ\text{C}$ , respectively. Splitting of metal particles can be obtained by reducing  $\text{Rh}_2\text{O}_3$  at low temperatures.

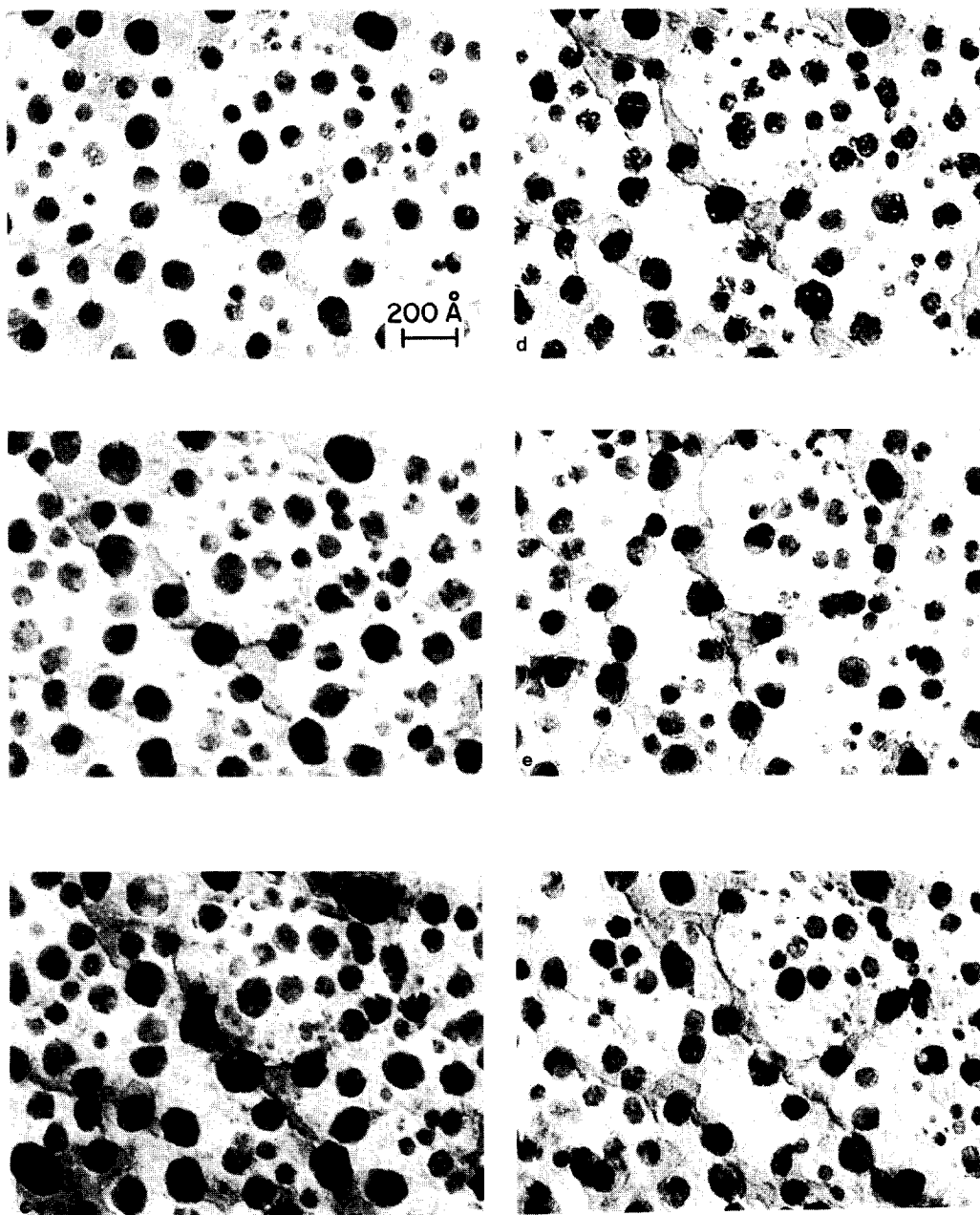


FIG. 2. Transmission electron micrographs showing the morphologies of Rh and  $\text{Rh}_2\text{O}_3$  particles supported on  $\gamma\text{-Al}_2\text{O}_3$ . The sample was heated sequentially (a) in  $\text{H}_2$  at  $600^\circ\text{C}$ , (b) in air at  $500^\circ\text{C}$ , (c) in air at  $600^\circ\text{C}$ , and then reduced in  $\text{H}_2$  at (d)  $150^\circ\text{C}$ , (e)  $450^\circ\text{C}$ , and (f)  $700^\circ\text{C}$ , each for 1 hr. Spreading of oxide after heating in air and splitting of metal particles by low-temperature reduction are similar to those for Rh on  $\text{SiO}_2$ , Fig. 1.

by regions of variable contrast which separate uniform contrast regions of single grains. After oxidation and reduction some of these particles move to the edges of multiautom steps in the  $\text{Al}_2\text{O}_3$ .

#### *Pt-Rh on Amorphous $\text{SiO}_2$*

A specimen of  $52 \pm 5\%$  Rh with an initial total film thickness of  $15 \text{ \AA}$  was heated in  $\text{H}_2$  at  $650^\circ\text{C}$  for 2 hr to form Pt-Rh alloy particles as shown in Fig. 3a. From X-ray photoelectron spectroscopy of these metals, to be described in a later publication, we conclude that Pt and Rh form a fairly uniform alloy at this composition. After heating in air at 500 and  $600^\circ\text{C}$ , Rh segregated from alloy crystallites and formed  $\text{Rh}_2\text{O}_3$  around the particles as shown in Figs. 3b and c.

Figures 3d to j show the morphology changes of the Pt-Rh alloy in reducing conditions. At low temperatures, 25 and  $75^\circ\text{C}$  (Figs. 3d and 3e), small crystallites  $10 \text{ \AA}$  in diameter appear at the edges of particles. This morphology presumably occurs because  $\text{Rh}_2\text{O}_3$  is at the edge of particles. After heating to  $150^\circ\text{C}$  (Fig. 3f), as in pure Rh, the splitting of particles is much more pronounced. As the alloy with a rhodium oxide layer around each particle is reduced, it generates some open channels between metal particles.

Most particles in Fig. 3f through i show distinct regions with different contrasts. The high contrast cores of most low-contrast particles are mainly Pt, while the edges are Rh metal. This should be observed even for a single-phase particle since Pt has a higher atomic number than Rh, and the ratio of atomic scattering factors for these two metals is  $\sim 1.4$ . The X-ray photoelectron spectrum also showed surface enrichment of Rh at these temperatures. Examination of Figs. 3d to g shows that the splitting of the particles occurred mostly at the outer, low-contrast region of each particle. The Pt cores remain rather uniform after all heat treatments.

The splitting of an alloy, unlike pure Rh, cannot be fully recovered even if the temperature is increased up to  $500^\circ\text{C}$ : cores remain darker than edges of particles. Only after heating to  $700^\circ\text{C}$  in  $\text{H}_2$  for 1 hr (Fig. 3j) do particles show uniform contrast and have hexagonal shapes like those in Fig. 3a. Thus, alloy particles coalesce only at  $\sim 500^\circ\text{C}$  and become uniform only at  $700^\circ\text{C}$ .

## DISCUSSION

### *Mechanisms of Redispersion*

Redispersion involves the formation of small particles from larger ones, a process which must counteract the increase in free energy which accompanies an increase in surface area (16). Thus, redispersion must be a multistep process because it is necessary to "freeze" the configuration obtained in an initial step to obtain a stable redispersed form. An alternate process occurs in SMSI in which for some metals on strongly interacting supports the surface area can be made to increase by heating in  $\text{H}_2$  (9). However, it should be noted that in SMSI the dispersed state is not simply smaller metal particles but is rather monatomic metal atoms forming strong chemical interactions with the support. These are not strictly metal particles because they do not chemisorb  $\text{H}_2$  and they exhibit chemical shifts suggesting negative electronic charge (17, 18).

We shall confine our discussion to the situation where large metal particles are transformed into smaller metal particles. While this could occur in a reducing atmosphere, the most probable processes involve cyclic treatment in  $\text{O}_2$  and  $\text{H}_2$  to oxidize and then reduce the particles.

*Atomic migration.* In this process atoms or molecules leave metal particles, migrate to other regions of the support, and form new particles. The mechanisms for these processes have been discussed most clearly by Wynnblatt and co-

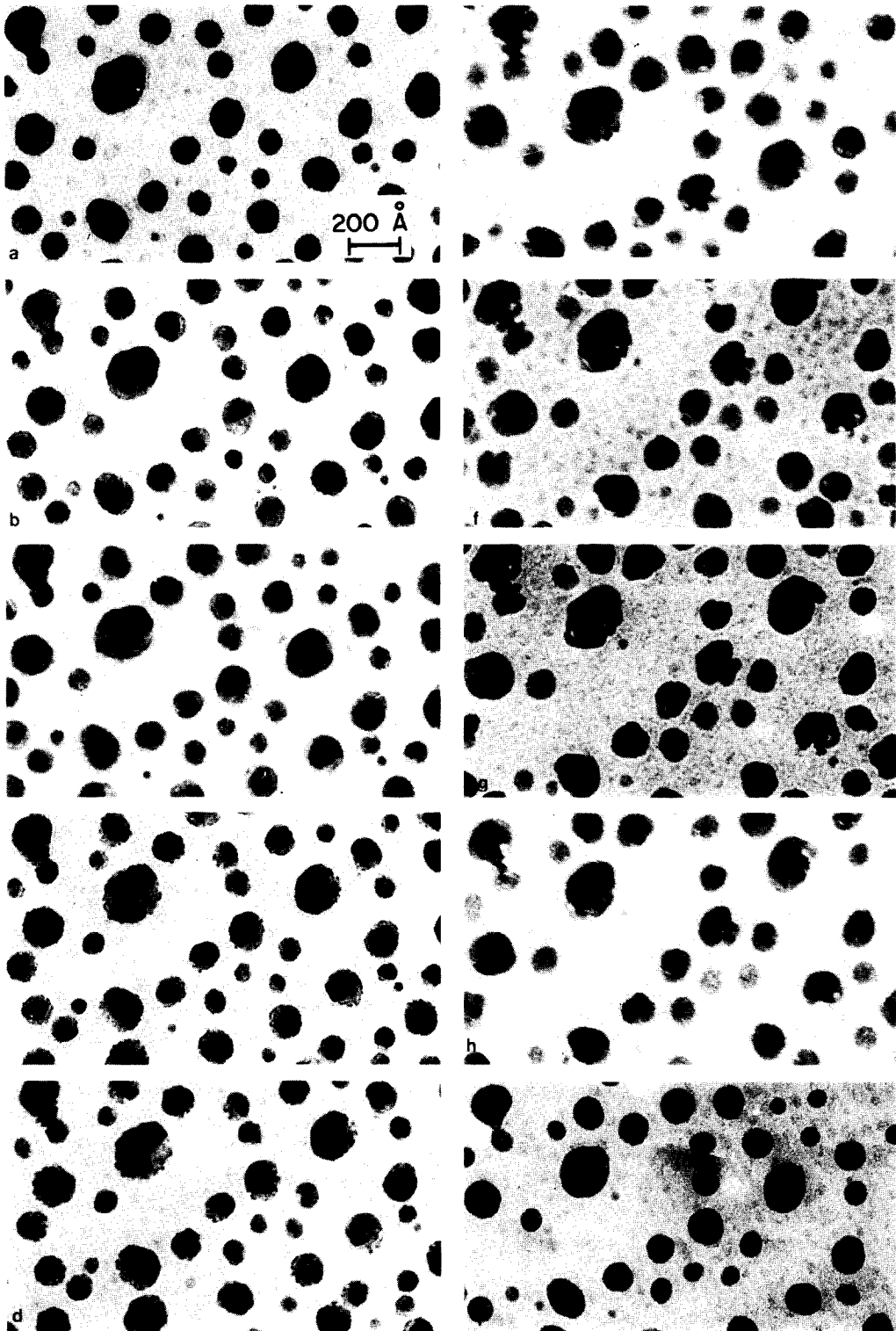
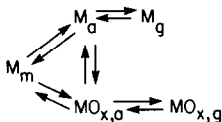


FIG. 3. Micrographs of 48% Pt-52% Rh alloy particles on  $\text{SiO}_2$  illustrating segregation and splitting of alloy particles when heated (a) in  $\text{H}_2$  at  $650^\circ\text{C}$ , (b) in air at  $500^\circ\text{C}$ , (c) in air at  $600^\circ\text{C}$ . This was followed by reduction in  $\text{H}_2$  at (d) room temperature, (e)  $75^\circ\text{C}$ , (f)  $150^\circ\text{C}$ , (g)  $250^\circ\text{C}$ , (h)  $350^\circ\text{C}$ , (i)  $500^\circ\text{C}$ , and (j)  $700^\circ\text{C}$ . The homogeneous alloy can only be recovered at temperatures of  $700^\circ\text{C}$ .

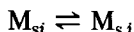
workers (5, 6). Basically one assumes that, upon heating, atoms or molecules are in equilibrium with particles,



where subscript m, a, and g represent metal particle, isolated atoms adsorbed on the substrate, and a gaseous species, respectively. In the absence of  $O_2$ , of course, no oxide species should form.

At high temperatures, equilibrium in these exothermic reactions shifts to the right (and up or down depending on  $H_2$  and  $O_2$  pressures). Now, if the temperature is rapidly lowered, it may be possible to "freeze" the concentration in the adsorbed or dilute phase,  $M_a$  or  $MO_{x,a}$ . Slight heating of  $H_2$  should then decompose the oxide (if any) and sinter the isolated atoms into smaller and clusters.

This process can only work if one does not have significant mass transfer between metal particles, because the process



will cause the larger particles to grow, where  $M_{si}$  and  $M_{sj}$  represent metal atoms in particles in  $i$  and  $j$ , respectively. This is just the atomic migration or Ostwald ripening mechanism of sintering. Thus, it must be assumed that equilibrium is established between a particle and the surface or gas around it, but that distances between particles are sufficiently large that the above transformation does not occur significantly. The vapor transport path which opens up in the presence of  $O_2$  may thus explain why one can achieve redispersion by heating in  $O_2$  but only sintering otherwise. It also may explain the absence of interparticle redispersion on planar supports by this mechanism: the particles are so close together that atoms migrate from one particle to another without forming an appreciable con-

centration of isolated atoms. Metal oxide vapor is also swept away from a planar support.

*Particle breakup.* The increase in surface area which we observe is apparently quite different than that involving atomic diffusion over the support or molecular diffusion in the vapor. In our case, a single particle breaks up into two or more smaller particles with no atoms observed to leave the parent particle. This process has been suggested by Ruckenstein and co-workers (7, 8) to occur for Pt on  $Al_2O_3$ . However, Wynnblatt and co-workers (5) were unable to reproduce their results, and they suggested that the mechanism proposed by Ruckenstein and co-workers was implausible. It should also be noted that with Pt the process suggested was not one of complete oxidation of Pt particles followed by reduction.

The present experiments indicate that redispersion can occur completely *within* individual particles. Oxidation of Rh produces an oxide particle which, upon reduction, forms a cluster of smaller particles, sometimes appearing as one or more cracks in the oxide particle.

In the following section we shall discuss the possible processes which produce the observed morphologies in oxidation and reduction.

#### *Morphology in Oxidation of a Small Particle*

In the present experiments when a Rh particle on  $SiO_2$  or  $Al_2O_3$  is oxidized, the oxide is observed to expand parallel to the surface upon heating above  $500^\circ C$ . This may arise partially from the lower density of the oxides compared to the metals, but the expansion is too large to be accounted for by this effect alone.

We proposed previously (12) that this may come from a stronger interaction energy of metal oxide with the substrate than that of the metal with the substrate. Equivalently, one says that the metal oxide "wets" the surface while the metal



does not. In this mechanism the interfacial energies provide the driving force to produce the observed oxide morphology.

Another mechanism for oxide spreading appears possible which does not require interfacial energy differences or a density difference. This relies only on the formation of oxide on a curved surface of a metal.

Oxides probably form in all of these systems mainly by cation diffusion at the temperatures employed here. At the metal-metal oxide interface, cations form and diffuse through the oxide film along with electrons to the metal oxide-oxygen interface. There  $O_2$  is converted to oxide by reacting with the electron. Oxide thus grows at the free surface of the oxide film with metal ions coming from the underlying metal. On a flat surface the oxide can recede as the metal leaves the interface. However, on a curved surface a void is necessarily created unless the oxide film can break up and collapse continuously on the receding metal.

The effect of a void produced in oxidation of a curved surface was elegantly demonstrated in sectioned micrographs of oxidizing iron wires and near the corner of an iron bar (15). As sketched in Figs. 4a and b, (drawn to scale from micrographs of Ref. (15)) the wire forms a void and growth ceases except where the oxide remains in contact with the metal. At a corner, the oxide layer is also much thinner than over a flat surface.

An identical situation may occur in oxidation of a small metal particle. Metal will be transported from the metal-metal-oxide interface in forming new oxide, and this *must* create a void at the interface which will stop further growth as sketched in Fig. 4c. Growth can only continue if a metal transport path exists from the metal particle to the metal oxide layer.

The obvious path for continued metal transport to form oxide for a particle on a support is *surface diffusion of metal over*

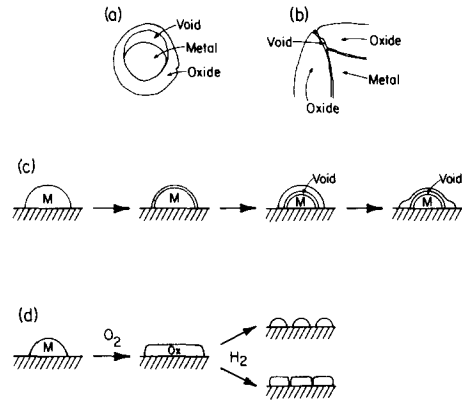


FIG. 4. Sketches showing cross sections of partially oxidized iron wire (a) and near the edge of a rectangular iron bar (b) after heating in oxygen from Ref. (15). Sketch (c) shows morphologies of small metal particles in oxidation. A void should be created at the interface of metal-metal oxide which stops further growth of oxide if oxide grows by cation migration. Further growth can only occur at the  $SiO_2$  interface. Sketch (d) shows the morphologies of small metal particles in oxidation-reduction cycle.

*the support*. Thus, after an initial period where a thin oxide film forms, oxide should grow only as metal can diffuse over the support. This should result in the spreading of the oxide as it continues to form, since only at the substrate junction can growth proceed indefinitely.

A number of possibilities are implied by this mechanism. First, the rate of oxidation may be much slower than on a flat surface, although the rate should initially be that of the flat surface until vacancies begin to form at the interface. The activation energy for reaction should also change as different mechanisms become operative. In different temperature regimes oxide may form by different mechanisms. If the energy to form a void is high, the process should slow down as vacancies form in the interface. The steady-state process could then occur only by simultaneous anion and cation diffusion which would have a slower rate. Second, the mechanism suggests that the oxide particle may have a "bubble" at its core after all metal has diffused out and

reacted, or, if the oxide film cracks, successive layers of oxide may form. These are, of course, only speculations because structures formed would be only a few angstroms in size, and rates of all transport paths, energetics, and elastic constants for metal and oxide are entirely unknown.

#### *Morphology in Reduction of an Oxide Particle*

The thin oxide particle found by oxidation is crystalline and consists of only a few grains, as shown by dark-field imaging (12). This particle is reduced to form smaller metal crystallites or a metal particle with cracks, as shown in Fig. 4d.

The simplest mechanism invokes the relative interfacial energies, or, equivalently, the decomposing oxide is assumed to "wet" the support while the forming metal does not. Of course, the process by which reduction occurs would have to be considered to explain the detailed structures. This involves nucleation of metal and surface and bulk diffusion of various species. We suggest that metal may form by nucleation of small crystallites with oxide decomposing completely by 150°C and crystallite sintering only at ~400°C.

Some particles exhibit gaps or cracks upon reduction. This is probably explainable by the ideas indicated above if a small number of metal nuclei form. Cracks could also be caused by elastic stresses in the reducing oxide. As reduction progresses, the density of the particle increases, and, since the metal oxide adheres strongly to the support, a tensile stress should develop in the oxide. This could result in one or more cracks, perhaps forming preferentially at grain boundaries in the oxide particle where reduction rates are faster and fracture stresses lower.

It is interesting to estimate the surface area increase produced by this cycle. If particles were cylinders and reduction produced a single cylinder, the diameters

before and after reduction (100 and 57 Å respectively) predict a surface area increase of 48%. If it is assumed that the original particle is transformed into close-packed cylinders of 30 Å diameter, then the surface area increases by 144%. These crude estimates indicate a size increase comparable to that produced in regeneration. The irregular shape of the small particles after reduction compared to the regular shape of the original particle should result in an even larger area increase than these estimations predict.

#### SUMMARY

These results appear to demonstrate clearly that an oxidation–reduction cycle can produce many smaller particles from larger ones. We have repeated these results for Ir on SiO<sub>2</sub> by treatments at slightly higher temperatures than those reported here for Rh. This process leads to a surface area increase estimated to be ≥100%, which represents significant redispersion.

This process should be capable of producing smaller particles for any metal which (1) can be oxidized and (2) can be reduced without sintering. Condition (1) is applicable to all metals except probably Pt. Condition (2) depends on the ability to decompose an oxide at a sufficiently low temperature that sintering does not occur. Metals which form very stable oxides and have high mobilities are thus not good candidates for this redispersion process. This is presumably why Pd could not be redispersed by an oxidation–reduction cycle. Metals such as Rh, Ir, and Ru are probably the best candidates since they have high melting points and weakly stable oxides.

It is interesting to note that compounds other than oxides may lead to redispersion by this process. Formation of sulfides, carbides, chlorides, etc. followed by hydrogen reduction could redisperse metal particles whose oxide stabilities

and reduction temperature make them unsuitable.

Morphologies of alloys exhibit additional complexities. Oxidation of Pt-Rh alloys forms  $\text{Rh}_2\text{O}_3$  at edges of particles by 600°C. Reduction of this  $\text{Rh}_2\text{O}_3$  to form tiny Rh particles is evident even at 25°C. The particles coalesce at 400°C, leaving a larger particle with Pt at its core and Rh at its periphery. Only at 700°C do particles appear to become uniform in composition. The ability of oxidation-reduction cycling to produce a surface excess of one species on an alloy particle also suggests interesting possibilities to produce a surface enriched in one species. We shall discuss this in detail in a future publication.

#### REFERENCES

1. Johnson, M. F. L., and Keith, C. D., *J. Phys. Chem.* **67**, 200 (1963).
2. Fiedorow, R. M. J., and Wanke, S. E., *J. Catal.* **43**, 34 (1976).
3. Fiedorow, R. M. J., Chahar, B. S., and Wanke, S. E., *J. Catal.* **51**, 193 (1978).
4. Ruckenstein, E., and Chu, Y. F., *J. Catal.* **59**, 109 (1979).
5. Stulga, J. E., Wynblatt, P., and Tien, J. K., *J. Catal.* **62**, 59 (1980).
6. Yao, H. C., Wynblatt, P., Sieg, M., and Plummer, H. K., Jr., "Sintering Processes." Plenum Press, New York, 1980.
7. Ruckenstein, E., and Malhotra, J. L., *J. Catal.* **41**, 303 (1976).
8. Dadyburjor, D. B., *J. Catal.* **57**, 504 (1979).
9. Baker, R. T. K., Prestridge, E. B., and Garten, R. L., *J. Catal.* **59**, 293 (1979).
10. Chen, M., and Schmidt, L. D., *J. Catal.* **55**, 348 (1978).
11. Chen, M., and Schmidt, L. D., *J. Catal.* **56**, 198 (1979).
12. Chen, M., Wang, T., and Schmidt, L. D., *J. Catal.* **60**, 356 (1979).
13. Wang, T., and Schmidt, L. D., *J. Catal.* **66**, 301 (1980).
14. Young, L., "Anodic Oxide Films." Academic Press, London/New York, 1961.
15. Engell, H. J., and Wever, F., *Acta Metallurg.* **5**, 695 (1957).
16. Anderson, J. R. "Structure of Metallic Catalysts." Academic Press, London/New York, 1975.
17. Tauster, S. J., and Fung, S. C., *J. Catal.* **55**, 29 (1978).
18. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., to be published.