

REFERENCES

1. ROONEY, J. J., AND PINK, R. C., *Proc. Chem. Soc.* **1961**, 70; *Trans. Faraday Soc.* **58**, 1632 (1962).
2. BROUWER, D. M., *Chem. Ind. (London)*, **1961**, 177; *J. Catal.* **1**, 372 (1962).
3. MUHA, G. M., *J. Phys. Chem.* **71**, 633 (1967); **71**, 641 (1967).
4. OKUDA, M., AND TACHIBANA, *Bull. Chem. Soc. Jap.* **33**, 863 (1960); ROBERTS, R. M., BARTER, C., AND STONE, H., *J. Phys. Chem.* **63**, 2077 (1959).
5. HIRSCHLER, A. E., NEIKAM, W. C., BARMBY, D. S., AND JAMES, R. L., *J. Catal.* **4**, 628 (1965).
6. CAVANAUGH, J. R., AND EPIFANIO, O. M., private communication.
7. HOWARTH, O. W., AND FRAENKEL, G. K., *J. Amer. Chem. Soc.* **88**, 4514 (1966).
8. EDLUND, O., KINELL, P.-O., LUND, A., AND SHIMIZU, A., *J. Chem. Phys.* **46**, 3679 (1967).
9. HULME, R., AND SYMONS, M. C. R., *Proc. Chem. Soc.* **1963**, 241; *J. Chem. Soc.* **1965**, 1120; see also, VINCOW, G., in "Radical Ions" (E. T. Kaiser and L. Kevan, eds.), Chap. 4. Wiley (Interscience), New York (1968).
10. DESSAU, R. M., SHIH, S., HEIBA, E. I., *J. Am. Chem. Soc.* **92**, 412 (1970).

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The Structure of Metallic Particles in Dispersed Catalysts

Metallic particles dispersed in silica have been used extensively for many decades as industrial catalysts and also for fundamental laboratory investigations (1). Their usefulness lies in their good thermal stability and the high surface area of the metal. In more recent years it has been suggested that the activity depends upon the sizes of the metallic particles to an extent that exceeds the change in surface area (2-7). For instance, the adsorption of nitrogen was found to depend more on crystal size (15-70 Å) than on the type of metal, and this led to the suggestion that the nature of the surface sites exposed on small crystals is important (3). Subsequently, models of small crystals have been examined and the distributions of the various types of site computed as a function of the sizes and shapes of the crystals (8, 9).

In all this work it has been assumed that the small crystals have a FCC structure. However, it has been shown by electron microscopy that for some FCC metals very small particles formed by condensation

from the vapor in a vacuum (10, 11), or as smokes in inert gas atmospheres (12), or by precipitation from solution (13), are not necessarily FCC crystals, but frequently adopt specific multiply-twinned forms. Several such types of particles have been identified by electron diffraction and dark-field electron microscopy, and they have been shown to contain 5 (pentagonal bipyramid) and 20 (icosahedron) uniform tetrahedral units, respectively (10). These forms, particularly the latter, are attractive because their structure allows them to expose only close-packed faces in a very compact manner.

The detailed internal structure of these multiply-twinned particles can be seen in very high-resolution electron micrographs by Komoda (14), and their stability has been investigated theoretically (15, 16). It was shown that for small numbers of atoms (about 500) a pentagonal bipyramid should be more stable than a tetrahedron, and that up to cluster sizes of about 2000 atoms, an icosahedron should be about as stable as a

FCC sphere. Thus theoretical considerations substantiated the thermodynamic stability of the multiply-twinned clusters and provided an explanation for their presence in very high proportions in deposits of small particles.

The metallic particles in highly dispersed supported catalysts are frequently in the size range which we have been considering above (10–100 Å). Therefore, it seems important to examine by electron microscopy particles of some FCC metals supported on silica, in an effort to determine whether they have an FCC or multiply-twinned structure. Multiple twinning can be recognized by a comparison of bright- and dark-field electron micrographs, because only a part of the multiply-twinned particle will appear bright in the dark-field image.

Icosahedral particles are the most common form of the multiply-twinned clusters (11). Because their shapes are close to spherical, it is not easy to distinguish them by their outline. Sometimes internal structure can be seen, but a better way to iden-

tify them is to obtain dark-field images with 111 diffracting beams. Then, because only two separated parts of the particle are diffracting, the image of each particle appears as a pair of spots, and in larger particles each spot can be resolved as a rhombus. The displacement between the spots is normal to the operating reciprocal lattice vector (11). This therefore provides a selective test for identifying such particles. The effect is demonstrated by the pair of bright- and dark-field micrographs in Fig. 1a,b. This specimen contains palladium crystals formed by condensation from the vapor onto mica in UHV under conditions for producing epitaxy. The bigger crystals have the normal FCC structure, but the dark-field image from a 111 reflection (Fig. 1b) picks out a set of 12 multiply-twinned particles (circled). The arrow shows the direction of the reciprocal lattice vector of the reflection used to obtain the dark-field image. In this case the crystals are well oriented, so that the splitting of the spots is in the same direction for all the crystals,

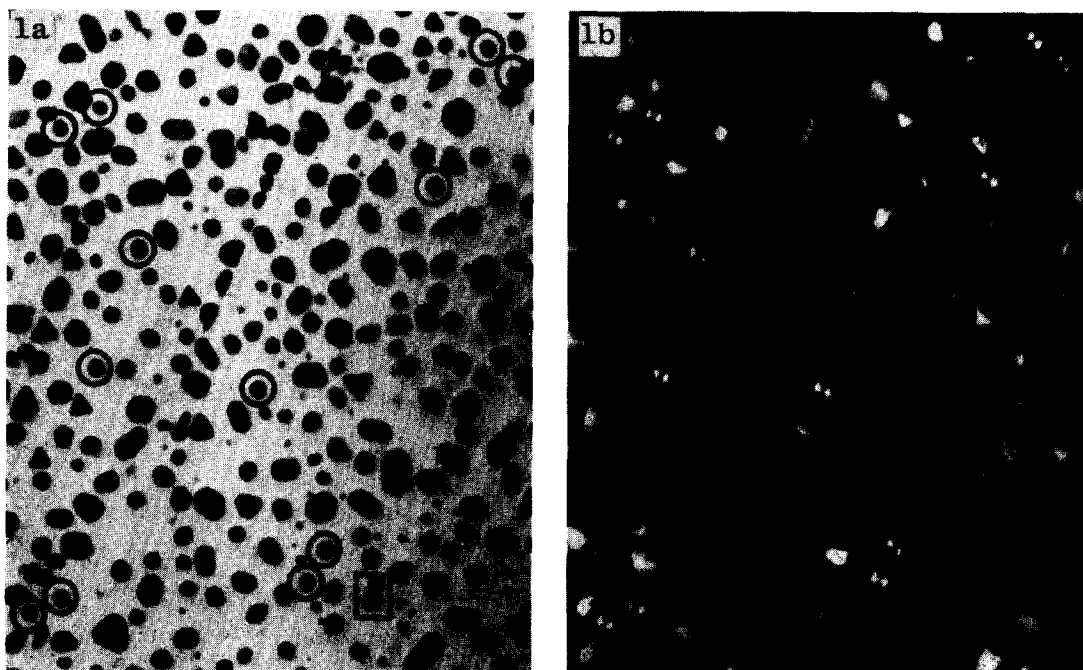


FIG. 1. Electron micrographs ($\times 280000$) of the same area containing palladium particles formed by condensation onto mica in UHV: (a) bright-field image; (b) dark-field image from 111 reflections with reciprocal lattice vectors in the direction of the arrow. The circled particles are identified as multiply-twinned icosahedra by the pairs of spots in the dark-field image. A pentagonal bipyramid is marked by a square in (a).

and the displacement between the pairs is normal to the direction of the operative reciprocal lattice vector.

An alternative form of a multiply-twinned particle is a pentagonal bipyramid (10-12), which can be recognized by its pentagonal outline and its internal contrast. Figure 1a contains the image of such a particle, marked by a square. It does not appear in the corresponding dark-field image (Fig. 1b) because none of its components is in a suitable orientation to give a diffracting beam through the objective aperture. In a field containing very small particles (~ 30 Å) pentagonal bipyramids would be more difficult to identify than their icosahedral counterparts.

We have used this technique of dark-field microscopy to examine some supported catalysts for the presence of multiply-twinned clusters. The metal dispersions were made by the method developed for preparing stable silica-supported metals which were translucent to infrared radiation (17).

Briefly, a solution of a suitable metallic salt was mixed with Aerosil 380 (70 Å particle size), dried in air at 100°C , and after being vacuum degassed at 150°C for 1 hr, reduced in hydrogen (10–15 Torr) at 300°C for another hour. The metal dispersions were designed to contain a metal/silica mole ratio of 1:20. Specimens suitable for electron microscopy were prepared either by shaking fine-meshed grids in the powder and examining particles adhering to the edges of the grid bars, or by dispersing the powder ultrasonically in methyl chloroform, and collecting some of the suspension on a carbon-coated grid.

Four metals were examined: Ni, Au, Pt, Pd. Of these, nickel was the least satisfactory for detailed examination because of the poor contrast from the metallic particles. Several different preparations of gold gave particle sizes in the range 100–350 Å; a few multiply-twinned particles were detected but the majority of the particles were single crystals of FCC structure. Plati-

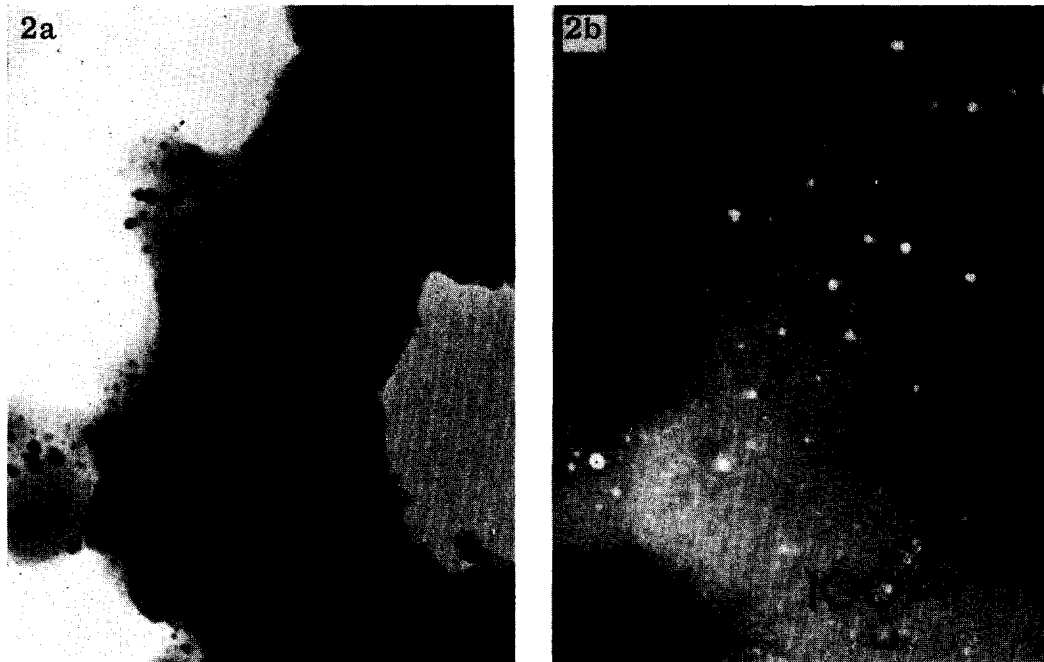


FIG. 2. Electron micrographs ($\times 280000$) of the same area of palladium particles dispersed on silica: (a) bright-field image; (b) dark-field image from (111) reflections with reciprocal lattice vectors within the arc between the arrows. Only three particles give pairs of spots (circled) consistent with multiply-twinned icosahedra. The size of the particles of silica is much greater here than initially (70 Å), because the silica sinters in the electron beam during the time taken to set up the dark-field conditions.

num and palladium, with particle sizes 10–80 and 20–100 Å, respectively, were examined in greater detail.

An example of a bright- and a dark-field image (111 reflections) from the same area of a Pd specimen is shown in Fig. 2. In this case there is no epitaxy, and hence the crystals have random orientations, and the 111 reflections produce a ring in the diffraction pattern. To form a dark-field image, an arc of this ring is transmitted through the objective aperture. The angular spread of these diffracted beams is shown in the bottom left-hand corner of Fig. 2b, and if any pairs of spots are from icosahedral multiple-twins, the normal to the directions of splitting should lie within this arc. In this field there are several pairs of closely-spaced spots (circled) which fulfill the criteria for multiply-twinned icosahedra. This is the greatest concentration which we have observed, and in most fields for palladium and platinum specimens, none could be detected. Many of the particles were too small for their outline to be clearly resolved. Of those which were sufficiently large, none showed any evidence for pentagonal structure. Furthermore careful comparison of the bright- and dark-field images showed that the diffracting areas of the particles in the dark-field image were essentially the same as the total projected area of the particle as shown by the bright-field image. This shows that most of the particles are single crystals with little evidence for multiple-twinning.

We conclude, therefore, that most of the metallic particles in supported catalysts prepared in this way are normal FCC crystals, and that less than 2% may be multiply-twinned.

REFERENCES

1. SCHUIT, G. G., AND VAN REIJEN, L. L., *Advan. Catal. Rel. Subj.* **10**, 242 (1958).
2. DORLING, T. A., AND MOSS, R. L., *J. Catal.* **5**, 111 (1966).
3. VAN HARDEVELD, R., AND VAN MONTFOORT, A., *Surface Sci.* **4**, 396 (1966).
4. CLARK, J. K. A., FARREN, G., AND RUBACOVA, H. E., *J. Phys. Chem.* **71**, 2376 (1967).
5. CARTER, J. L., CUSUMANO, J. A., AND SINFELD, J. H., *J. Phys. Chem.* **70**, 2257 (1966).
6. BOUDART, M., ALDAG, A. W., PTAK, C. D., AND BENSON, J. E., *J. Catal.* **11**, 35 (1968).
7. CORMAK, D., AND MOSS, R. L., *J. Catal.* **13**, 1 (1969).
8. VAN HARDEFELD, R., AND HARTOG, F., *Surface Sci.* **15**, 189 (1969).
9. MOSS, R. L., *Platinum Metals Rev.* **11**, 141 (1967).
10. INO, S., AND OGAWA, S., *J. Phys. Soc. Jap.* **22**, 1365 (1967).
11. ALLPRESS, J. G., AND SANDERS, J. V., *Surface Sci.* **7**, 1 (1967).
12. KIMOTO, K., AND NISHIDA, I., *J. Phys. Soc. Jap.* **22**, 940 (1967).
13. BOTTOMS, W. R., AND MORRIS, R. H., presented: *25th Annu. Electron Microscope Soc. Amer. Meet.* (1967).
14. KOMODA, T., *Jap. J. Appl. Phys.* **7**, 27 (1968).
15. FUKANO, Y., AND WAYMAN, C. M., *J. Appl. Phys.* **40**, 1656 (1969).
16. ALLPRESS, J. G., AND SANDERS, J. V., *Aust. J. Phys.* **23**, 23 (1970).
17. EISCHENS, R. P., PLISKIN, W. A., AND FRANCIS, S. A., *J. Chem. Phys.* **22**, 1786 (1954).

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