JOURNAL OF CATALYSIS 40, 379–382 (1975)

Crystallite Size and Dispersion of Platinum in an Alumina Matrix

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Received June 3, 1975

A method for preparing thin sections of platinum on alumina reforming catalysts has been developed. The platinum particle size distribution and the degree of dispersion has been determined by transmission electron microscopy. There is agreement with the average crystallite size determined from X-ray diffraction line broadening. The morphology of the alumina matrix is also revealed.

INTRODUCTION

Highly dispersed platinum in a matrix such as alumina or silica is widely used as a catalyst for many reactions. Many techniques have been employed to determine the nature, structure, morphology, particle size, and dispersion of the platinum in these catalysts. This information is necessary for the interpretation of their catalytic activity. The surface area of supported platinum by the selective adsorption of H_2, O_2, and CO has been studied (*1–12*). Electron microscopic techniques to determine dispersion and particle size distribution of the platinum have been developed (*5,8–10,13*).

Adams *et al.* (*5*) used a sample containing 1.25% platinum. The sample was dispersed in butyl alcohol by ultrasonic treatment and evaporated on a carbon grid. Films of catalyst mulled in a solution of collodion in amyl acetate were supported on 200-mesh copper grids and carbon coated (*9,10*). The platinum concentration varied from 1.83 to 2.8%. Platinum particle size distribution in the catalyst was difficult to obtain because of the sample preparation techniques. Many investigators (*1,2,5,6*) found that the average platinum particle size as determined by chemisorption of gases such as H_2, O_2, and CO was lower than that determined by X-ray line broadening techniques. The sensitivity of these X-ray diffraction methods was too low to detect small platinum particles. In order to increase the sensitivity of the determination of platinum crystallite size by X-ray line broadening, acetyl acetone was used to extract the alumina and concentrate the platinum (*14*). For a normal distribution of crystallite sizes the line profile is a Cauchy relation. In aged catalysts where crystallite growth has taken place, the X-ray diffraction line profile is the sum of profiles due to multimodal crystallite size distributions. The composite profile may be deconvoluted to give the various average crystallite size distributions. A surface weighted mean crystallite size may be obtained by a Fourier analysis of the line profile (*15,16*). The application of correction procedures to obtain a ripple-free size distribution curve resulted in a complete characterization of the state of platinum dispersion in the catalyst (*17*).

The object of the present work was to determine platinum crystallite size distribution and the degree of platinum dis-

persion in a catalyst as well as the morphology of the matrix by preparing thin sections and obtaining electron micrographs of these sections.

EXPERIMENTAL

The principle of sectioning thin slices of a hard inorganic oxide involves embedding it in a matrix of essentially the same hardness. Usually a glass knife will suffice to slice the matrix with catalyst dispersed throughout it but with hard alumina the glass knife will be easily damaged. A du-Pont diamond knife with a large angle, 55°, proved satisfactory.

Engelhard RD 150 catalyst containing 0.35% platinum was reduced in a hydrogen atmosphere and the catalyst was maintained at 500°C for 2 hr in a stream of hydrogen before cooling in a helium atmosphere. This reduced most of the platinum to platinum metal. This catalyst sample was finely dispersed in Epon 812 and cast in capsules to form a pointed cylinder. An LKB microtome equipped with a DuPont

FIG. 1. Electron micrograph of a thin section of Engelhard RD 150 catalyst (magnification 109,000×).

FIG. 2. Electron micrograph of thin section of Engelhard RD 150 catalyst (magnification 405,000×).

55° angle diamond knife was used to section thin slices. The thickness of the slices is determined from thermal expansion and were 1000 Å. The slices were floated on water and picked up on Athene screens and examined with an RCA Model EMU3E electron microscope.

MORPHOLOGY OF ALUMINA MATRIX

Transmission electron micrographs (Fig. 1) of thin sections of Engelhard RD 150 catalyst show a highly porous structure with evidence of sections of well-defined crystals indicating a layer effect due to dehydration. The morphology of the bayerite crystals is preserved on calcination with the layer structure generated by dehydration.

PLATINUM CRYSTALLITE SIZE AND DISTRIBUTION

Transmission electron microscopy of uniform thin sections of Engelhard RD 150 catalyst showed a uniform distribution of darker spots indicating particles of higher density. An electron micrograph of a catalyst section is shown in Fig. 2. The diagonal striations are knife marks. All the dark spots are not in focus due to the thickness of the film and the depth of focus of the electron microscope. The platinum particles are spherical, as indicated by the dark spots, and are uniformly distributed throughout the section.

Based on a platinum concentration of 0.35% and a density of 1.3 g/ml for the

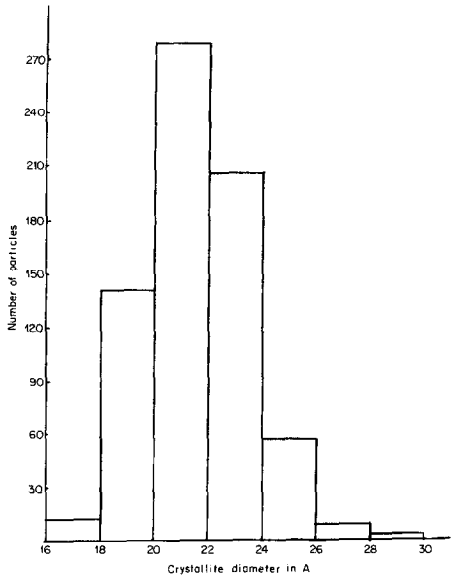

FIG. 3. Particle size distribution for RD 150 catalyst.

catalyst and a platinum crystallite size of 21.5 Å, the number of particles in the volume represented by 1-cm^2 area at a magnification of 450,000× in Fig. 2 is calculated to be 11 and agrees quite well with the number of darker spots seen in the micrograph.

An analysis of the size of 708 particles is given in Fig. 3. The resolution of the electron microscope is 7 Å and the size of the particles varied from 16 to 30 Å in diameter with an average of 21.5 Å. This compares with the value of 22 Å obtained from an X-ray line broadening analysis of an acetyl acetone extraction (*14*) of the same catalyst. The same average diameter was determined from the analysis of the 111, 200, 220, and 311 lines indicating spherical particles.

REFERENCES

1. Spinadel, L., and Boudart, M., *J. Phys. Chem.* **64**, 204 (1960).
2. Adler, S. F., and Keavney, J. J., *J. Phys. Chem.* **64**, 208 (1960).
3. Pliskin, W. A., and Eischens, R. P., *Div. Petroleum Chem. Boston* **4**, C25, 1959.
4. Mills, G. A., Weller, S., and Cornelius, E. B., *Actes Congr. Int. Catal. 2nd 1960* **2**, 2221, 1961.
5. Adams, C. R., Benesi, H. A., Curtis, R. M., and Meisenheimer, R. G., *J. Catal.* **1**, 336 (1962).
6. Hughes, T. R., Houston, R. J., and Sieg, R. P., *Ind. Eng. Chem.* **1**, 96 (1962).
7. Gruber, H. L., *J. Phys. Chem.* **66**, 48 (1962).
8. Dorling, T. A., and Moss, R. L., *Catalysis* **7**, 378 (1967).
9. Wilson, G. R., and Hall, W. K., *Catalysis* **17**, 190 (1970).
10. Freel, J. J., *Catalysis* **25**, 139; 149 (1972).
11. Bett, J., Kinoshita, K., Routsis, K., and Stonehart, P., *J. Catal.* **29**, 160 (1973).
12. Ratnasamy, P., Leonard, H. J., Rodrique, L., and Fripiat, J. J., *J. Catal.* **29**, 374 (1973).
13. Benesi, H. A., Curtis, R. M., and Studer, H. P., *J. Catal.* **10**, 328 (1968).
14. Plank, C. J., Kokotailo, G. T., and Drake, L. C., American Chemical Society Conference, Chicago, Illinois, Sept. 1961.
15. Bertaut, E. F., *Acta Crystallogr.* **3**, 14 (1950).
16. Warren, B. E., and Averbach, B. L., *J. Appl. Phys.* **21**, 595 (1950).
17. Pausescu, P., Manaila, R., Popescu, M., and Jijovici, E., *J. Appl. Crystallogr.* **7**, 281 (1974).