The Structure of Supported Platinum Catalysts

EXAMINATION BY ELECTRON MICROSCOPY

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Modern techniques are steadily increasing our knowledge of the structure and properties of the supported platinum metal catalysts so widely used in chemical processing. The main function of the support, such as charcoal, alumina or silica, is to increase the surface area of the platinum metal and so to enhance catalyst performance, and methods for studying the dispersion of the platinum are therefore of considerable importance. This article describes the application of electron microscopy to the problem and compares the results given by this and other methods.

The study of the state of dispersion of the metal in supported platinum catalysts is based on indirect methods such as gas chemisorption, and on direct methods such as X-ray diffraction and electron microscopy. The chemisorption method depends on finding conditions of temperature and pressure at which a gas—hydrogen or carbon monoxide—will chemisorb to monolayer coverage on the platinum but not on the support. The volume of gas taken up shows the extent to which the platinum has been dispersed. For example, it was shown (1) that a freshly prepared reforming catalyst (0.6 wt. per cent platinum on η-alumina) had most of the platinum atoms exposed, probably as islands or as very small crystallites less than 10 Å in size. There is, however, a growing awareness that the performance of supported

metal catalysts (diffusion limitations apart) may be related not only to the metal area but to the actual size of the metal crystallites responsible for that area. The latest standard electron microscopes can resolve the smallest aggregates of platinum atoms which may be described as crystallites and hence provide valuable information on the sizes and numbers of crystallites present. Further, the distribution of platinum throughout the support and characteristics of the support itself may be examined.

Appearance under the Electron Microscope

Suitable specimens for electron microscopy can be prepared by cutting extremely thin sections (300 to 500 Å) with an ultra-microtome from catalyst particles embedded in, for example, "Araldite". An alternative method is ultrasonic dispersion of the catalyst in butyl alcohol. Remembering the very small area under examination, a number of specimens must be prepared and surveyed in order to obtain representative electron micrographs.
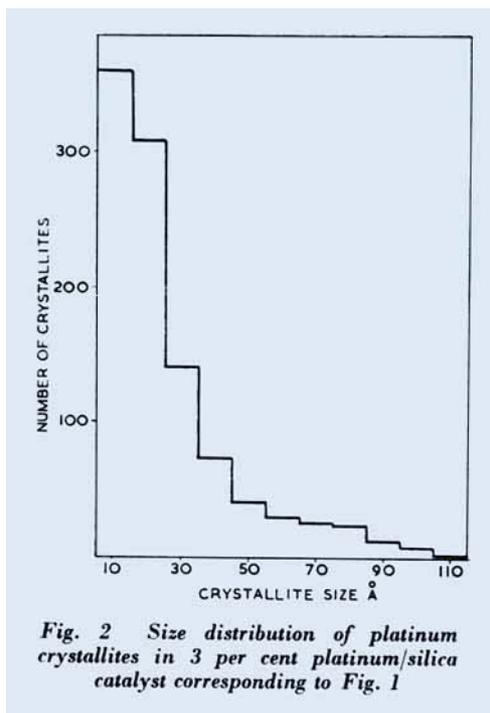
Platinum/Silica

Fig. 1 shows an electron micrograph of a 3 per cent platinum/silica catalyst made by impregnating silica gel with chloroplatinic acid solution, drying at 120°C and reducing in hydrogen. At a magnification of 100,000 ×, the platinum shows up as dark spots evenly distributed as minute crystallites in the pore system of the silica gel. Electron diffraction patterns from selected areas with a high
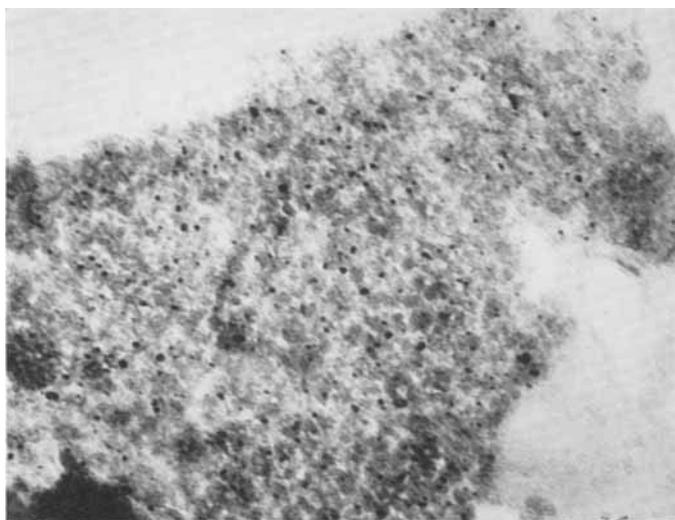
concentration of dark spots confirm the presence of platinum.

About 1000 platinum crystallites in this electron micrograph were sized in terms of their diameters, since they appear approximately spherical, in increments of 10 Å, and Fig. 2 shows the number of crystallites observed in each size range. The crystallites are predominantly in sizes below about 50 Å; in the 10 Å size crystallites most of the atoms ($d_{atomic} = 2.77$ Å) are "surface" atoms. Although the 10 to 50 Å crystallites account for only one-quarter of the total weight of platinum present on the support, nevertheless they provide almost half of the available platinum area. Hence the platinum primarily responsible for the performance of this supported catalyst can be "seen" by electron microscopy.

Electron micrographs of the silica support itself showed spherical particles of, very roughly, 100 Å diameter. Assuming no loss of area when the particles contact, the calculated surface area is ∼250 m²/g. This rapid estimate agrees reasonably with the BET gas adsorption value.

Fig. 2 Size distribution of platinum crystallites in 3 per cent platinum/silica catalyst corresponding to Fig. 1

Platinum/Charcoal or Alumina

Fig. 3 shows an electron micrograph of a platinum on charcoal catalyst at a magnification of 100,000 ×. Chemisorption methods showed the very high platinum area of a Johnson Matthey 5 per cent platinum/ charcoal catalyst which formed the basis of the sample examined. The catalyst was then subjected to a vigorous sintering treatment (firing at 300°C in air) to encourage crystallite growth. Nevertheless, as the electron micrograph shows, the platinum crystallites were

Fig. 3 5 per cent platinum/ charcoal catalyst, heated in air at 300°C, magnification 100,000 ×, showing very small platinum crystallites
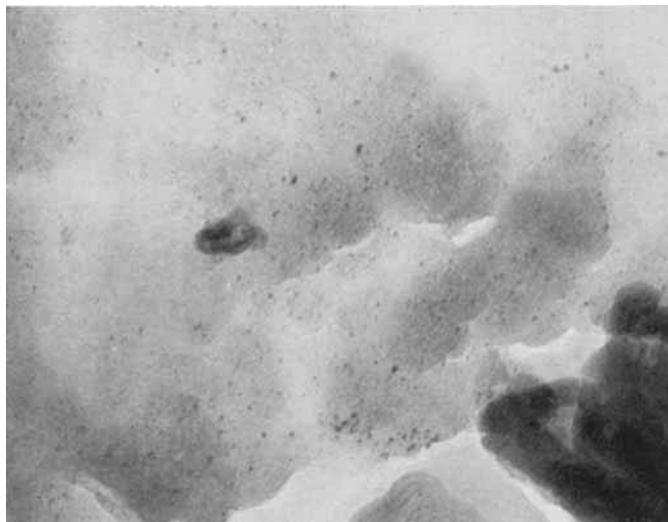
still very numerous and extremely small in size, yielding a large catalytically-active platinum surface.

Fig. 4 shows an electron micrograph (35,000 ×) of a catalyst with 2.5 per cent platinum supported on a low-area alumina. Measurement of the platinum area by carbon monoxide chemisorption showed that it was closely similar to the area of the platinum/silica catalyst discussed above (Fig. 1), but the electron micrographs are in marked contrast. Whereas the platinum crystallites in the silica-supported catalyst are widely distributed, this alumina-supported catalyst shows dark patches of platinum. At still higher magnifications (100,000 ×), these patches were clearly resolved as groups of small platinum crystallites (Fig. 5) and the platinum area is obviously higher than it might at first seem.

Comparison with Chemisorption and X-ray Diffraction

The chemisorption method for measuring the metal area of a supported catalyst has already been briefly discussed. Its main problems are:

chemisorbing gas on the metal but not on the support;

choice of a criterion for monolayer coverage;

the relation existing between the number of gas molecules adsorbed at this point and the number of surface metal atoms.

The equipment required (2), however, is relatively simple, for example, a conventional volumetric apparatus such as might be used for BET surface area determinations, a vacuum micro-balance or a flow system linked to a gas chromatograph. If the observed metal area is S, the mean crystallite size, d_s, is calculated from $d_s = 6/S\rho$ where ρ is the density of the metal; it is assumed that the crystallites are spheres or any regular polyhedron except the tetrahedron. This diameter, d_s, is the surface-average diameter defined by $\Sigma n_i d_i^3/\Sigma n_i d_i^2$, where there are n_i crystallites of diameter, d_i. From the crystallite size distribution (Fig. 2) obtained from electron micrographs the diameter, d_s, is readily calculated for comparison with the mean size obtained by chemisorption.

The determination of crystallite size by X-ray diffraction depends on the fact that below about 1000 Å size, X-ray reflections are broadened beyond the normal "instrumental" breadth. Thus the method involves measuring the breadth of one or more X-ray reflections, preferably using an X-ray counter-diffractometer which provides a chart-recording of the position, profile and intensity of each reflection. The Scherrer equation relates
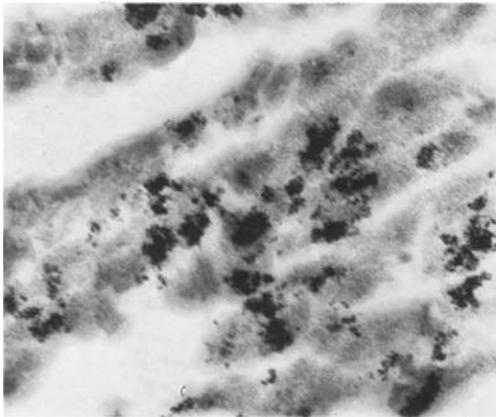
Fig. 4 A 2.5 per cent platinum/alumina catalyst, magnification 35,000 ×, showing platinum as dark patches
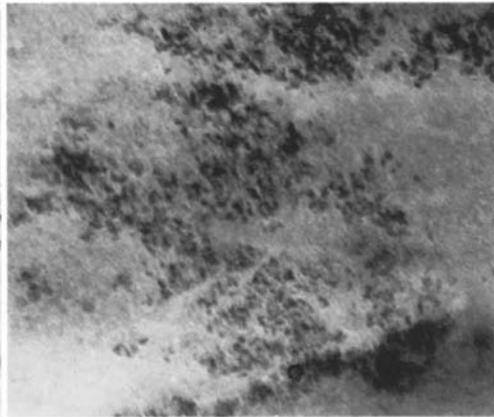

Fig. 5 Same catalyst, magnification 100,000 ×, resolving individual platinum crystallites

the excess breadth to the mean crystallite size, d_v, which is a volume-weighted average diameter, $\Sigma n_i d_i^4 / \Sigma n_i d_i^3$. Again, this type of average diameter can be calculated from electron microscope observations for comparison with X-ray results. The main problems with the X-ray diffraction method are:

> the smaller platinum crystallites, perhaps those less than 50 Å, when measured with standard equipment, are not detected yet provide much of the available platinum area of the catalyst. The proportion of platinum remaining undetected can, however, be estimated (3);

> crystallite size is measured whereas the platinum can be present as particles, that is, agglomerates of crystallites, with interior surfaces inaccessible to gas molecules.

With the problems involved in measuring crystallite size (and platinum area) by chemisorption or X-ray diffraction, it is therefore of some interest to compare such results with the crystallite size distribution obtained from electron micrographs. This has been done for the 3 per cent platinum/silica catalyst (Figs. 1 and 2), taking into account the different types of average involved, with the results shown in the table. Some satisfactory conclusions can be drawn from these results:

> the assumptions involved in the chemisorption method (carbon monoxide at 25°C, CO/Pt ratio=1, no adsorption on silica) seem reasonably justified;

> the electron microscope resolved most of the platinum crystallites contributing to the platinum area;

> the 'particles' viewed in the electron microscope were also the crystallites detected by X-ray diffraction.

Relation to Catalyst Performance

There are two important consequences, at least, for catalyst performance arising from an increase in crystallite size, perhaps as a result of sintering during use.

The more obvious is the rapid loss in metal area accompanying crystallite growth. The

| Average Crystallite Size in 3 per cent Platinum-Silica Catalyst	
Mean diameter, d_s, of all crystallites:	
by chemisorption	45 Å
by electron microscopy	55 Å
Mean diameter, d_v, of crystallites 50 Å size and above:	
by X-ray diffraction	60 Å
by electron microscopy	65 Å

Fig. 6 Models of small platinum crystallites: left-hand represents approximately 10 Å diameter with mainly (111) crystal planes exposed; right-hand represents approximately 12 Å with predominantly (100) planes exposed
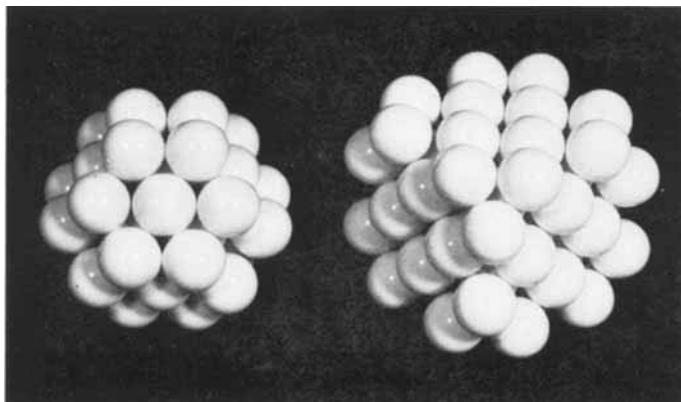
left-hand model in Fig. 6 represents a very small crystallite, $\sim$ 10 Å diameter, containing 38 atoms of which 31 are exposed (82 per cent), excluding those which only contact the support. The slightly larger right-hand model, $\sim$ 12 Å diameter, represents 62 atoms but now only 44 (71 per cent) are present at the surface. One important factor in choosing the support material is the stability which it can impart to the crystallites against sintering together.

Further reference to the models (Fig. 6) shows a less obvious consequence of crystallite growth. Whereas the smaller crystallite displays mainly (111) crystal planes, addition of a single layer of atoms to form the slightly larger crystallite yields a surface with predominantly (100) planes exposed. As these small crystallites grow, other crystal planes and atomic arrangements rapidly form and change, each with its characteristic catalytic properties. For example, when *n*-heptane was reformed over a series of platinum/alumina catalysts (4), dehydrocyclisation activity was decreased and isomerisation increased as the mean crystallite size varied from 10 to 450 Å.

Some applications of the electron-microscope to supported catalyst research are therefore apparent.

(i) When the performance of a supported catalyst is being assessed, often the metal area is measured in order to report the specific activity, that is, activity per unit metal area. Now a further step forward would be to record the structure of the catalyst, at least in part, by determining the crystallite size distribution from electron micrographs.

(ii) Apart from duofunctional reforming catalysts where both platinum and alumina provide catalytically active sites, it is believed that the specific activity may sometimes be altered by the nature of the support. This means that, in addition to its traditional roles which include extending the metal area, the support co-operates somehow in the catalytic process. However, changing the support can alter the crystallite size distribution and again electron micrographs may help to disentangle the effects of crystallite size and support on catalyst performance.

Acknowledgement

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