

Small Particles of the Platinum Metals

THEIR PREPARATION, CHARACTERISATION AND USE IN CATALYSIS

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The economic use of noble metals as catalysts usually requires them to be in the form of extremely small particles, typically less than 100 Å in size. This article reviews methods for the preparation and characterisation of such particles, and their importance in catalysis. For certain limited classes of reaction, activity per unit of surface area is itself a function of particle size; possible bases for explaining this effect are discussed.

When using noble metals as catalysts, it is naturally desirable to employ them in a form such that the largest possible fraction of the atoms are at the surface and hence available to the reactants. This can only be achieved by converting them into very small particles having a high surface to volume ratio. Fortunately this can readily be done by the well-known techniques for preparing supported metal catalysts, which typically contain metal particles between 10 and 100 Å in size. Reasons for being able to make small particles in this way will be given later. There are two other methods which have been used for preparing particles in this size range.

- (i) It is quite easy to make colloidal dispersions of metal particles, and these have some limited practical uses as catalysts.
- (ii) Small particles can also be made by evaporation of metal atoms from heated wires, and allowing them to condense on a cold surface: the technique has been used in fundamental catalytic studies (1).

Uniform Sphere Model

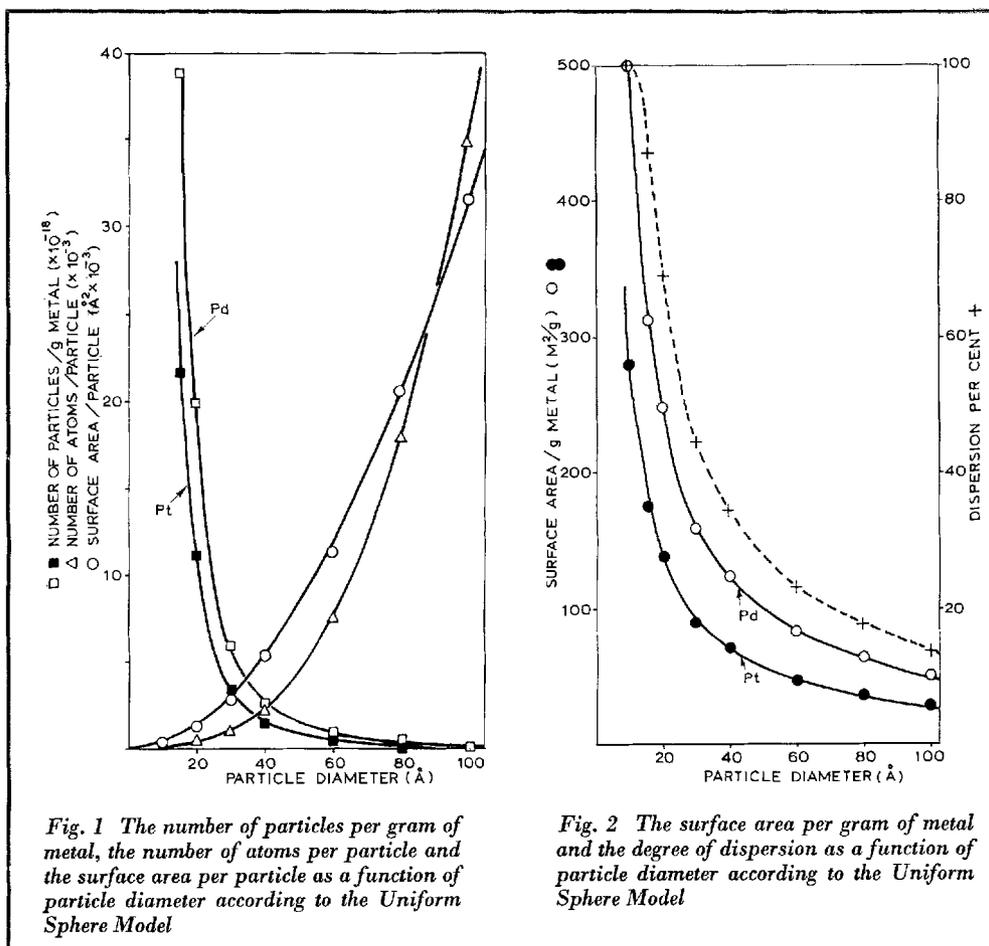
It is helpful to begin by establishing quantitatively the dependence of surface

area on particle size. We do this by a simple model in which we consider 1 g of metal in the form of small spheres of uniform radius r ; then using well-known formulae the surface area and volume of a single sphere are readily calculated as a function of r . Assuming the particles to have the normal density of the metal, the volume is converted into a mass, and hence the number of particles per g of metal is derived. Using the relations

$$n_a = m/m_a = mN/\mu$$

where n_a is the number of atoms of mass m_a in a particle of mass m , and N is Avogadro's constant and μ the atomic mass relative to ^{12}C , the number of atoms in a single particle can be calculated. Finally the total surface area per g is obtained as the product of the area of each individual particle and the number present.

The results of calculations made for palladium and platinum using this Uniform Sphere Model are shown in Figs. 1 and 2. The area per particle naturally increases as the square of the diameter, and the number of atoms per particle as its cube. The number of particles per g is therefore an inverse cubic relation, and the total area per g varies as the simple reciprocal of the diameter. Because of the nearly twofold difference in density



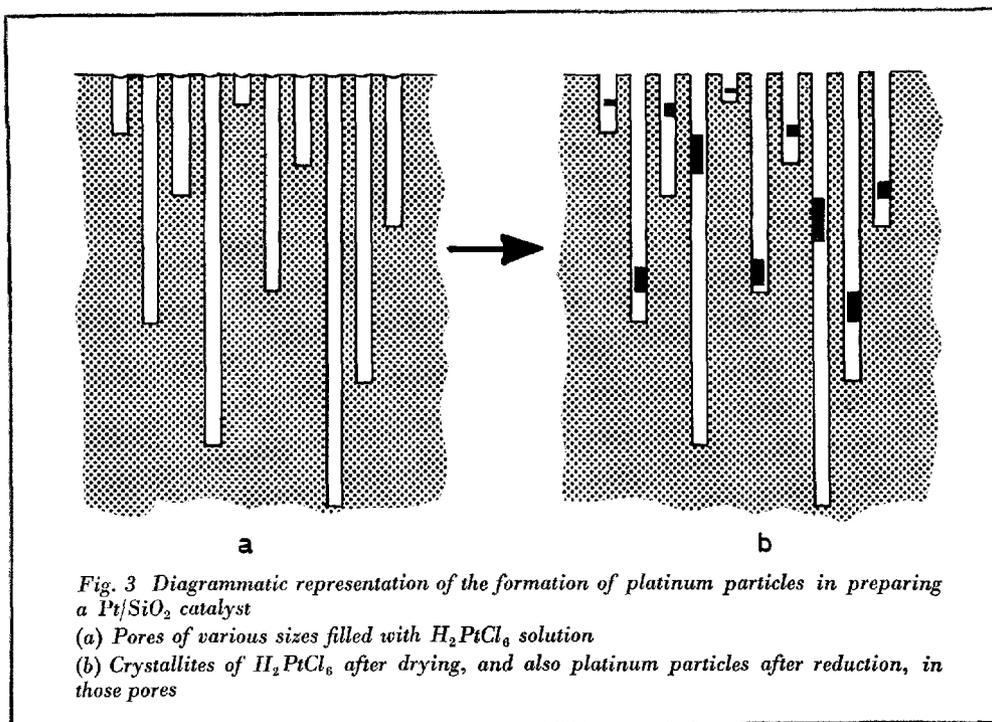
and in atomic mass between the two metals, palladium particles of a given size are much lighter than platinum particles of the same size; 1 g of palladium therefore produces almost twice as many particles of a given size as does platinum, with a consequently greater surface area. Such calculations are useful in a semiquantitative way, but they make no assumptions concerning crystal geometry and therefore lose significance for extremely small particles. It is also of course quite unrealistic to suppose that in real catalysts all the particles would have the same size; to assume that they are approximately spherical may be more reasonable.

Another measure of the effectiveness of subdividing metal into small particles which is

sometimes used is the percentage of atoms present on the surface: this is termed the *degree of dispersion* D , and its dependence on particle size is shown in Fig. 2. To estimate the number of atoms at the surface of a particle, it is necessary to assume what area a single atom would occupy. We suppose that the whole surface comprises the closely-packed (111) plane, in which the area of a single platinum atom would be 6.55 \AA^2 . Since the atomic radii of palladium and platinum are very similar, the dependence of dispersion on size is almost exactly the same for the two metals. The relevant relations are

$$D = n_s/n_a = a/n_a \times 6.55$$

where n_s is the number of atoms at the surface of a particle of surface area a .



Preparation of Small Metal Particles

As noted above, conventional methods for making supported metal catalysts frequently lead to metal particles smaller than about 100 Å in size (2). We may distinguish between two different ways in which they can arise. When the support is quite unreactive towards the metal compound employed (e.g. silica gel and chloroplatinic acid), impregnation of the support with a solution of the metal compound, followed by drying, gives microcrystals of the compound in each physically separate pore. The size of these microcrystals will thus depend on the volume of the pore in which they are formed on evaporation of water during drying, and on the concentration of the solution used. Thus with an amorphous support such as silica gel, the presence of a wide distribution of pore sizes naturally leads to a wide distribution of metal particle sizes on reduction of the microcrystals of the metal compound (3). The effect is illustrated schematically in

Fig. 3. In such systems the average metal particle size can be altered by changing the pore characteristics, by changing the metal loading and by sintering.

When a reactive support is used in conjunction with a suitable metal-containing species (e.g. activated carbon and PdCl₄⁻), a chemical reaction takes place whose nature is poorly understood but is probably a kind of hydrolysis. Small particles of metal are obtained on reduction (4) because the existence of a large number of reactive centres on the support, acting as nuclei, and the limited amount of metal-containing species available, means that each nucleus cannot grow to be large. Chemical pretreatment of the support, as well as the concentration of the solution used, can thus affect average particle size. Ion exchange procedures also lead to highly dispersed metals (3, 5).

A similar principle applies to the preparation of metal sols containing very small particles. Success depends on forming a large number of nuclei in the nucleation phase, and

subsequently allowing these to grow in the presence of a limited supply of metal salt. Colloidal platinum having an average size of about 20 Å (Fig. 4) is readily prepared by reduction of a dilute solution of chloroplatinic acid with sodium citrate at 100°C (6). Colloidal palladium has also been made and deposited on boehmite (AlO(OH)) filaments for catalytic use (7).

There is much interest in the preparation of extremely small metal particles, where it is more meaningful to speak in terms of a *cluster* of a relatively few atoms than of a particle size. Thus the careful reduction of the chloroplatinate ion confined within a zeolite cage gives platinum clusters containing only about six atoms: they have high catalytic activity more reminiscent of iridium than of platinum, and hence are thought to be electron-deficient (8). Another approach which is receiving attention is the use of polynuclear metal carbonyls for the preparation of catalysts (9).

Characterisation

A number of experimental methods are available to give an estimate of the average size of small metal particles (10), but comparatively few give information on the size distribution. By far the best and most direct method is transmission electron microscopy, since this is the only technique to yield the images of the particles in a visible form (2). The method, which is fairly simple, involves dispersing a supported metal catalyst in a thermosetting resin, and then cutting with a microtome to give slices of about 1000 Å thickness. Metal colloids may be examined just by allowing a drop to evaporate on to a film of suitable material placed on the grid which goes into the sample holder. To obtain clear images of very small particles is not easy: good voltage stability and minimal instrumental vibration are required. In principle a size distribution is obtained by measuring a statistically significant number of particles (2, 3).

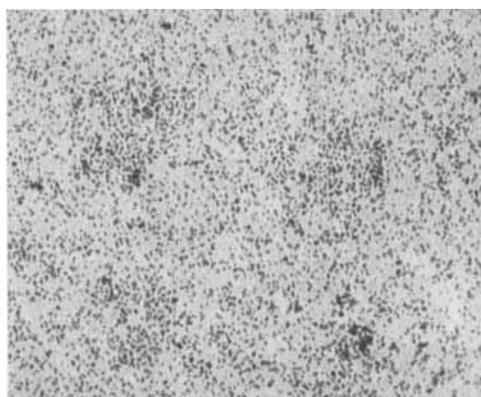
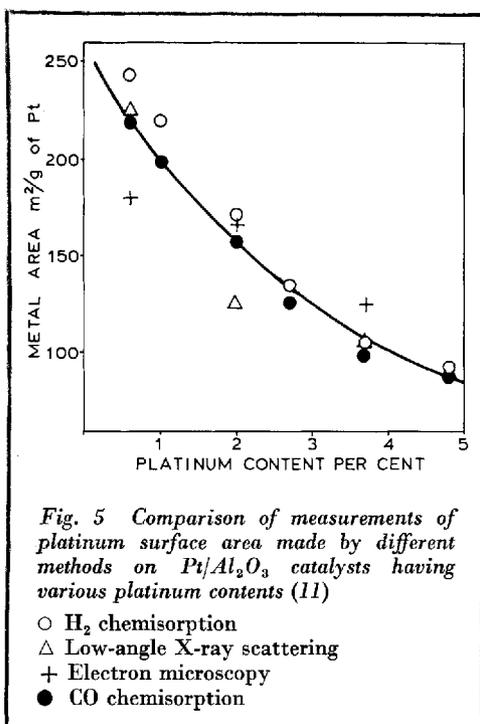


Fig. 4 Electron micrograph of colloidal platinum prepared by reduction of H_2PtCl_6 solution with sodium citrate (6). 1 mm = 50 Å

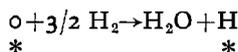
X-ray methods are also widely used, but the line broadening method is limited in scope since particles smaller than 40 to 50 Å are essentially amorphous to X-rays. Small-angle scattering of X-rays is a more promising technique, but the apparatus is costly and not yet widely available (11).

The selective chemisorption method has also been widely practised (8). Its success depends, in the case of a supported metal catalyst, on being able to remove pre-adsorbed gases, especially oxygen, from the surface of the metal particles without causing sintering, and then treating a gas whose molecules chemisorb selectively on the metal but not on the support. Measuring of the monolayer volume, and assuming what number of surface atoms each adsorbed molecule covers, allows an estimate of surface area and hence of average particle size. Hydrogen, oxygen and carbon monoxide have been successfully used. Unlike the physical methods mentioned above, this chemical method becomes increasingly sensitive with decrease in particle size, but residual uncertainty concerning the stoichiometry of the chemisorption especially for very small particles is an undoubted limitation. However, as Fig. 5 shows, careful work can yield surprisingly good agreement between results given by chemical and



physical methods, especially when the metal content is relatively large (11).

Consideration is also being given to gas titration methods. The first to be developed was the hydrogen-oxygen titration (12, 13, 14): the reaction monitored is basically:

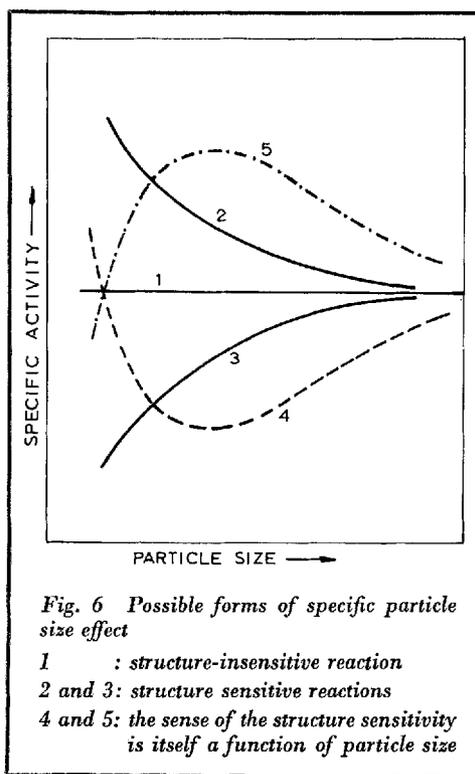


which gives a "magnification factor" of three compared with hydrogen chemisorption, but there has been much debate (15, 16) on the O/H ratio per site and on its variation with particle size. More recently adsorbed oxygen has been titrated with carbon monoxide (17), and adsorbed hydrogen with an olefin (18), the latter yielding added information on the time-dependence of the process.

Specific Particle Size Effects: Topographical Basis

It has long been thought likely that catalytic activity expressed per unit surface area (termed the *specific activity*) might itself be dependent on particle size, and much work

has been undertaken in recent years to look for *specific particle size effects*. All catalysts and all reactions need not behave in the same way, and Fig. 6 illustrates a number of possible ways in which specific activity might vary with particle size. The predicted basis for such effects is to be found in a careful examination of the surface topography of minute particles having one of the crystal habits appropriate to the face-centred cubic structure in which palladium and platinum crystallise (19). Let us consider first a small octahedron (Fig. 7): the surface atoms are of three quite distinct kinds, viz. corner atoms having four near neighbours (C₄), edge atoms with seven (C₇) and atoms within the (111) planes having nine near neighbours (C₉). It is evident that the fraction of surface atoms being at corners will decline rapidly as the size of the octahedron is increased, since the number of corner atoms (six) does not change. Similarly the fraction of edge atoms on the surface decreases with increasing size, but



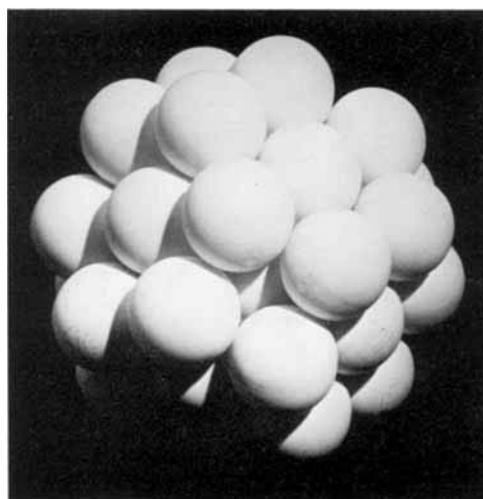
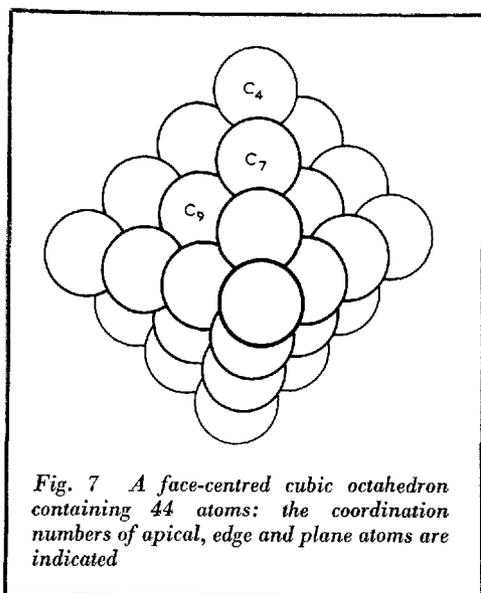
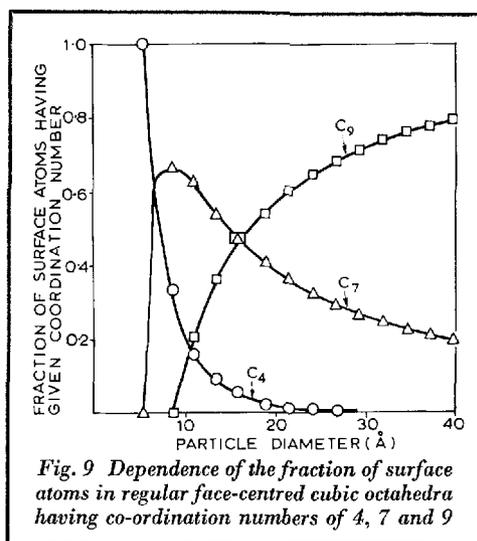


Fig. 8 A regular face-centred cubic cubo-octahedron containing 38 atoms

less rapidly; and the proportion of atoms with the (111) planes increases. One only has to ascribe different catalytic properties to each kind of surface atom to have a basis for specific particle size effects.

Several groups of workers have calculated the proportion of surface atoms having a given coordination number C_n as a function of particle size for regular crystals of various geometries (octahedra, cubo-octahedra (see Fig. 8), tetrahedra, etc.) (20-23): the results for fcc octahedra, shown in Fig. 9, take the expected form. The range of particle size from 8 to 40 Å has been termed the *mitohedral region* (23) for it is in this range that the proportions of atoms having low coordination number changes most rapidly with particle size. It is, however, quite improbable that a real catalyst particle will contain exactly the number of atoms required for a regular crystallite of any geometry; the average real particle will doubtless possess an incomplete outer shell of atoms. Fig. 10 illustrates a cubo-octahedron with an incomplete outer layer. Under these circumstances, atoms having coordination numbers other than those found in the perfect body will exist, and moreover special groupings of atoms or *sites* will occur which are not to be found at the

surface of perfect crystallites. Much emphasis has been laid on two particular kinds of site comprising five atoms and occurring at steps on (100) and (111) planes respectively; they have been strongly indicated as the sites for strong physical adsorption of nitrogen (24). B_5 sites at steps on a (110) plane are shown in close-up in Fig. 11. Somorjai (25) has also produced a great deal of clear experimental evidence for the extraordinary activity of atoms at steps on single crystal surfaces. Now the maximum surface density



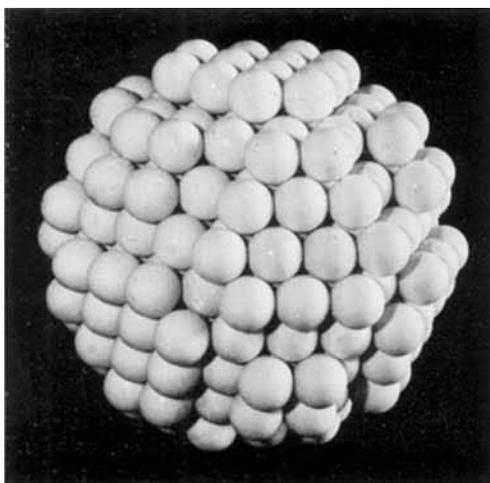


Fig. 10 An incomplete face-centred cubic cubo-octahedron showing B_5 sites at the junctions of (110) and (111) planes (courtesy of Dutch State Mines)

of B_5 sites arises just before each outer layer of atoms is completed (see Fig. 10). Calculations on incomplete cubo-octahedra (22, 24) having maximal numbers of B_5 sites, and of various sizes, have shown that the proportion of surface atoms comprising B_5 sites passes through a maximum when the particle size is between 20 and 25 Å, that is, in the middle of the mitohedrical region. Thus it is still possible to have a basis for specific particle size effects even with real (i.e. incomplete) particles.

It has recently been claimed (26, 27) that very small metal particles may not necessarily

show the symmetry expected from the bulk structure. Calculations have indicated that particles based on fivefold symmetry (icosahedra) are more stable than other forms, and indeed such forms have been observed. There is nothing inherently improbable in this notion, for five-coordinate complexes of the platinum metals are certainly known. It seems likely that fivefold symmetry particles are most easily formed under conditions of supersaturation, for example, in the hot wire evaporation method, and do not necessarily arise in the preparation of supported catalysts. Clusters of five rhodium atoms on silica have however been directly observed by electron microscopy (28).

Physical Properties

Since in very small particles a large fraction of the atoms are superficial and hence lack their proper complement of neighbours, it is reasonable to expect measurable differences in physical properties from those of the bulk solid. There is both theoretical and experimental evidence to show that melting point falls as particle size decreases, and a 10 Å particle may have a melting point of only half that of the bulk metal (27). Surface atoms are also calculated to have a much larger vibrational amplitude than sub-surface atoms, notwithstanding the fact that interatomic distances are shorter in the surface, by about

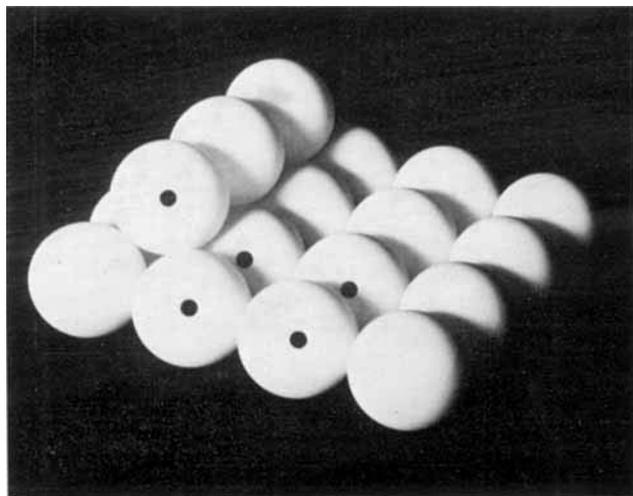


Fig. 11 B_5 sites at a step on a (110) surface: the atoms forming the nearest B_5 site are marked

3 per cent for a 10 Å particle. Surface pre-melting may also occur, and the molten surface skin on quenching may afford an amorphous outer layer. Such has indeed been observed recently for supported platinum particles examined by the radial electron distribution technique (29). Specific particle size effects may therefore well have an energetic as well as a topographical basis.

Specific Particle Size Effects: Experimental Evidence

To obtain accurate experimental evidence on the existence or otherwise of a dependence of specific activity on particle size is a matter of great difficulty, a major stumbling block being that supported metal catalysts normally contain a wide distribution of particle sizes. Furthermore it may be necessary to go to sizes below 20 Å to reveal the existence of such effects, and this has not always been done. To facilitate further discussion, it is desirable to introduce Boudart's terminology (30): a system exhibiting no dependence of specific activity on particle size is termed *structure-insensitive* (line 1 in Fig. 6); one exhibiting a dependence in either sense (curves 2 and 3 of Fig. 6) is referred to as *structure-sensitive*.

It is possible to summarise a large body of experimental work by saying that surprisingly few systems show structure sensitivity (30); the reason for this is not at the moment clear. One general class of reactions does however frequently reveal structure sensitivity, this being where carbon-carbon single bonds are broken in the presence of hydrogen, viz. hydrogenolysis or skeletal isomerisation. Specific activity usually increases with decreasing size (31), but the results obtained (32) for the hydrogenolysis of ethane over rhodium catalysts is of particular interest in that a maximum specific activity was observed for particles of about 10 to 20 Å in size, thus replicating the form of curve 5 in Fig. 6 (see Fig. 12). It has also been shown recently that the oxidation of ammonia on supported platinum catalysts shows structure sensitivity in the sense of specific activity becoming

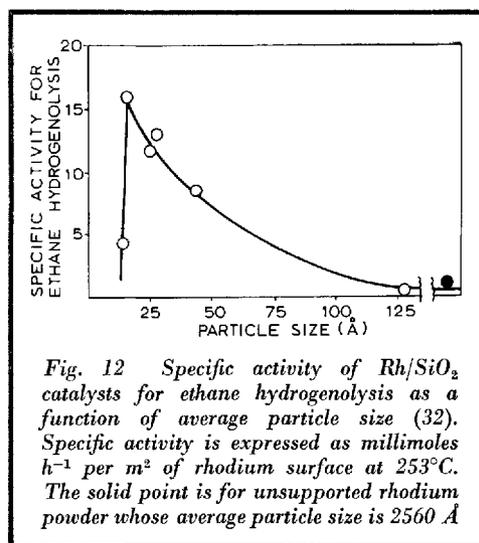


Fig. 12 Specific activity of Rh/SiO₂ catalysts for ethane hydrogenolysis as a function of average particle size (32). Specific activity is expressed as millimoles h⁻¹ per m² of rhodium surface at 253°C. The solid point is for unsupported rhodium powder whose average particle size is 2560 Å

larger with increasing particle size (33). This may however be associated with changes in the chemisorption strength or stoichiometry with changing particle size. The exchange of benzene with deuterium over iridium catalysts is also dependent on particle size (22).

Fundamental Calculations on Metal Clusters

Apart from the practical importance of using the platinum metals in a highly dispersed state, and of knowing whether or not a particular system is structure-sensitive so that particle size can be optimised for the envisaged application, there is lively current interest in this field because it is now possible to carry out fundamental quantum-mechanical calculations on small clusters of metal atoms. This is an advance of great potential significance, as for the first time it may prove possible to relate catalytic behaviour to basic electronic characteristics of the solid. Extended Hückel calculations on clusters of up to 55 atoms of palladium, silver, gold and palladium-silver have been reported (34), and the use of the self-consistent field X α method for eight-atom clusters of nickel and copper have also been described (35). Rapid and useful developments in this area are confidently to be expected.

Conclusion

The absence of widespread structure-sensitivity for many systems of practical importance is in fact a great blessing to the practitioner of catalysis, for it means that apart from simply maximising surface area there are no other factors to worry about in connection with particle size control. At the same time, the number of systems as yet investigated thoroughly is quite small, and further work may reveal more examples of structure-sensitivity: their advent would permit not only more rapid progress to be made in our understanding of heterogeneous catalysis, but also the manufacture of catalysts optimised with respect to particle size

for demanding reactions. It needs to be emphasized that the methods currently used for catalyst preparation are still relatively crude, and the performance of resulting catalysts still somewhat uncertain. We have much to learn from enzymes, whose specific activity and selectivity are vastly greater. If catalysis is to fulfil the hopes which are being placed on it, we must strive more effectively to emulate nature.

Future advances will depend much on our ability to prepare catalysts having much narrower particle size distributions than have hitherto been available: their advent would enable rapid progress to be made in our understanding of catalysis.

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