Macroscopic Aggregation in Palladium Blacks

OPTIMISATION OF CATALYTIC AND SORPTIVE PROPERTIES

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The basic particles of palladium blacks have been observed to cluster into macroscopic aggregates. Hydrogen treatment increases remarkably both the extent and degree of ordering of these aggregates. This may result in a substantial percentage of their surface areas being unavailable for adsorption. A theoretical model is proposed to account for the effects of this phenomenon in these and other unsupported and supported catalysts. Its predictions can be used to optimise their surface area and activity.

Microscopic aggregation or sintering involves the clustering of atoms. It is well known that this increases the size of the basic particles and thus the physical properties (1), the sorptive properties (2) and the catalytic properties (3) of materials. Macroscopic aggregates are the result of the clustering of these basic particles and their effects upon the activity of a catalyst have not been considered previously.

Macroscopic aggregation has been studied in five palladium black samples denoted A, B, C, D, and E. These samples, which were prepared by Johnson Matthey & Co. Limited, contained widely differing average particle sizes (A: 141 nm; B: 69 nm; C: 16 nm; D: 14 nm; E: 7 nm) (4, 5). Figure 1 shows a macroscopic aggregate in palladium black A, which is typical of those found in all untreated palladium blacks. It is readily seen that macroscopic aggregates are relatively large open-structured ensembles of basic particles. These aggregates can be defined in terms of the average coordination number, N, for each particle, the average size, 2R, of each particle (R equals the radius of a basic particle which is spherical), and the number, n, of constituent particles.

The simplest macroscopic aggregate, involving two basic particles in contact at point X, is illustrated in Fig. 2. It is clear that molecules of thickness d normal to the surface of the particles cannot adsorb in the area bounded by B, B', C and C'. This surface area of each particle that is unavailable for adsorption, S_{NON}, is given by $2\pi R^2 \times [d/(R+d)]$ (5). It can readily be shown (5)
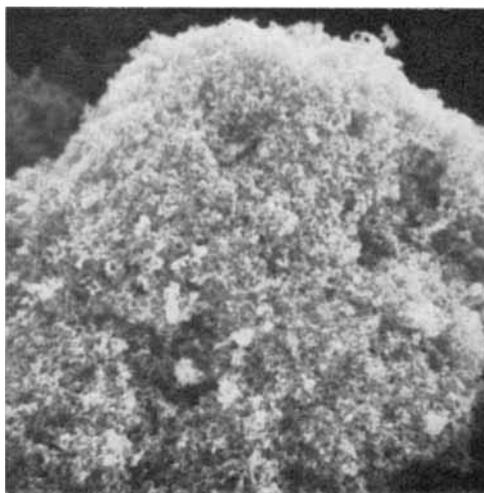

Fig. 1 A scanning electron micrograph of the untreated palladium black sample A (R=70.5 nm) ×7600

that in general the percentage surface area unavailable for adsorption by these molecules is given by $50N/(K+1)$, where K is the ratio R/d. This percentage increases as N increases, R decreases or d increases. Despite this and an abundance of other theoretical predictions (6) of the effects of macroscopic aggregation upon the surface area available for adsorption, little evidence exists (7) for such effects. This is presumably due to the low values of N normally found in aggregates (7) and other random packed beds (8), or to high ratios R/d that are unfavourable for detection.

Palladium Aggregates after Hydrogen Treatment

Hydrogen pretreatment of the palladium blacks at temperatures between ambient and 60°C caused each of the samples to form a single macroscopic aggregate. Figure 3 shows
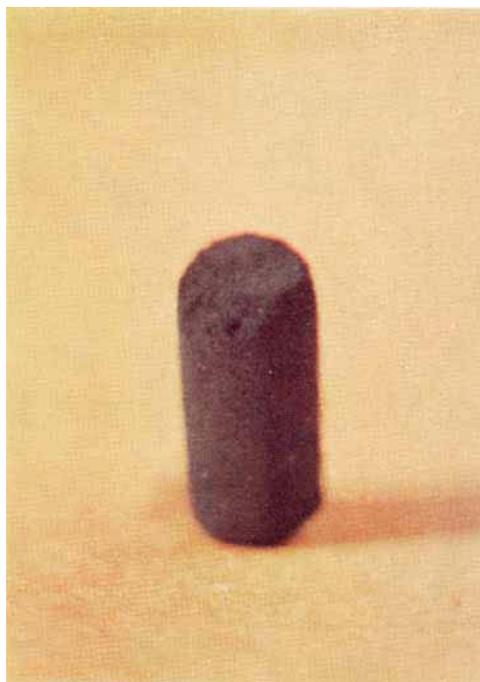

Fig. 3 *A single macroscopic aggregate (0.6 cm × 0.6 cm × 1.0 cm) formed on treating palladium black sample C (R=8 nm) with hydrogen at 50°C for two hours*

such an aggregate (0.6 cm × 0.6 cm × 1.0 cm) formed by palladium black C, containing basic particles 8 nm in radius. It is clear that this mild hydrogen treatment caused a remarkable increase in the extent of macroscopic aggregation. However, very little agitation (mechanical or ultrasonic) of an aggregate resulted (4) in its disintegration and thus the bonding between basic particles in the aggregates was not strong. It may be that these interparticular chemical bonds or menisci (4, 9) are formed at the local temperatures produced on the surface of the particles during the hydrogen treatment of these blacks which possessed oxidised surfaces.

Sorptive and Catalytic Effects of Aggregation

Hydrogen chemisorption at ambient temperature has shown (4) that no sintering occurs in the samples during hydrogen treatment at temperatures up to 60°C. Now nitrogen
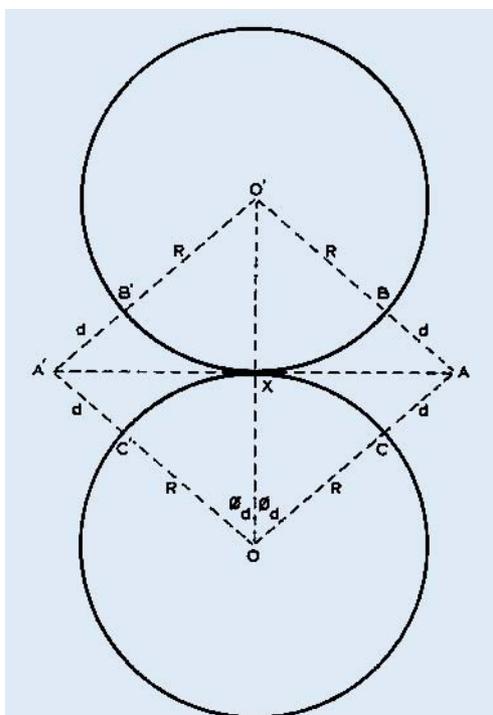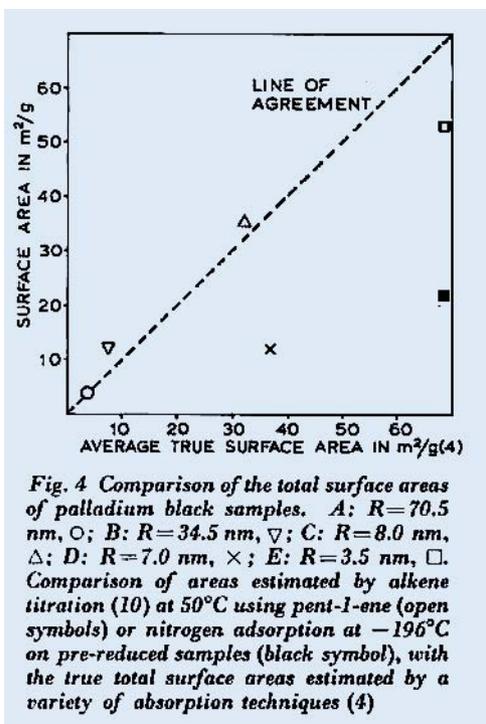

Fig. 2 *A cross-section through the simplest macroscopic aggregate, involving two particles in contact. The symbols are explained in the text*

Fig. 4 Comparison of the total surface areas of palladium black samples. A: R=70.5 nm, ○; B: R=34.5 nm, ▽; C: R=8.0 nm, △; D: R=7.0 nm, ×; E: R=3.5 nm, □. Comparison of areas estimated by alkene titration (10) at 50°C using pent-1-ene (open symbols) or nitrogen adsorption at −196°C on pre-reduced samples (black symbol), with the true total surface areas estimated by a variety of absorption techniques (4)

adsorption (4) at −196°C and alkene titration (10) at 50°C have been used to estimate the surface areas available for adsorption of nitrogen and pent-1-ene in a series of palladium blacks which had been subjected to this mild hydrogen pretreatment and which had formed single macroscopic aggregates. Their estimates of the total surface area are compared with the true surface areas of the samples in Fig. 4. From this it is seen that the total surface areas estimated for black D (by alkene titration) is only 35 per cent of its true surface area and that the surface area for black E is only 37 per cent (by nitrogen adsorption) or 70 per cent (by alkene titration) of its true surface area. Since it is known that under the conditions used no sintering occurred, these differences in surface area must be the result of macroscopic aggregation.

Assuming that the thicknesses, d, normal to the surface of nitrogen at −196°C and of pent-1-ene at 50°C are 0.35 (11) and 0.81 nm (5) respectively, and knowing that these two palladium samples have average particle

radii, R, of 7 nm (black D) and 3.5 nm (black E) (4), the value of R/d or K can be determined for each adsorbate/adsorbent system. Experimental values of the percentage surface area which is unavailable for adsorption equal $50N/(K+1)$ and substituting in the corresponding estimates of K we find that within experimental error N has the values of 12 (data for black D estimated by alkene titration and data for black E estimated by nitrogen adsorption) and 3 (data for black E estimated by alkene titration).

Twelve is the maximum value of the average coordination number N and corresponds to close-packing of basic particles within the macroscopic aggregates. This is the first time that such high coordination numbers have been found in unsupported adsorbents or catalysts. The value of N in untreated samples is known (5) to be low and therefore it follows that the mild hydrogen pretreatment induces a high degree of ordering in the macroscopic aggregates in addition to increasing the extent of the phenomenon.

Despite the effects of macroscopic aggregation upon the surface area available for adsorption, no effect upon the ability of these blacks to catalyse the hydrogenation/isomerisation of pent-1-ene has been detected (5).

Optimisation of Specific Surface Area and Activity

Macroscopic aggregation after hydrogen pretreatment has been shown to cause a significant diminution of the specific surface area which is available for adsorption in a series of palladium blacks. It follows that it also reduces their activity per unit weight. The effects of the phenomenon increase as N increases, R decreases or d increases.

Although the phenomenon has been observed for a series of palladium blacks, it undoubtedly occurs in other unsupported catalysts and even in supported catalysts (12). Let us consider if it is possible to maximise the surface area, and hence activity, of a catalyst using the model of macroscopic aggregation postulated here.
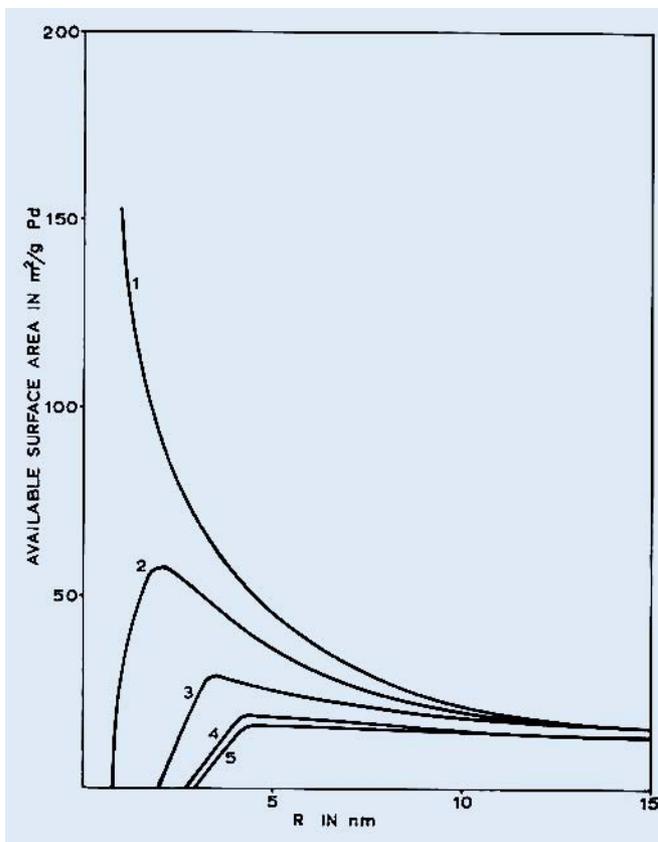
Fig. 5 The specific surface area of unsupported palladium that is available for adsorption by molecules of length d normal to the surface, assuming N is 12. 1: d=0.07 nm; 2: d=0.2 nm: 3: d = 0.4 nm; 4: d=0.57 nm; 5: d=0.6 nm. Similar sets of curves can be drawn for other values of N and for other materials

As an example, in Fig. 5 the surface areas per gram of palladium $(4\pi R^2 - N.S_{NON}).n$, where n is the number of constituent particles $n = 3/(4\rho\pi R^3)$ (5) and ρ is the particle density, are plotted as a function of R for various values of d, assuming N is twelve. It is normally assumed that, in the absence of special adsorption sites at certain values of R(2), decreasing the value of R always increases the specific surface area available for adsorption and thus the activity of the catalyst. However, it can be seen in Fig. 5 that the available surface area goes through a maximum at $R_{S_{max}}$ determined by the size of the adsorbate molecule. It is only if R is greater than $R_{S_{max}}$, that the specific surface area does indeed increase with decreasing R, but below $R_{S_{max}}$ decreasing R has the opposite effect. Therefore, the maximum available surface area and thus maximum

activity for a catalyst is given for any adsorbate at $R_{S_{max}}$.

If we calculate (5) approximate values of d for pent-1-ene, stilbene, ethylene and methanol to be 0.81, 0.57, 0.50 (13) and 0.07 nm, then for palladium samples exhibiting maximum macroscopic aggregation (N=12), $R_{S_{max}}$ has the values 7, 4.5, 3.5 and less than 1 nm respectively. Thus for a palladium black required for the hydrogenation of pent-1-ene, the hydrogenation of stilbene in the liquid-phase (14), the hydrogenation of ethylene or as the electro-catalyst for the reforming of methanol in a fuel cell (15), it would be disadvantageous to decrease the average particle size of the catalyst below 14, 9, 7 and about 1 nm respectively. Clearly, whether macroscopic aggregation must be considered an important factor when designing a catalyst of optimum surface area and activity depends

upon the size of the adsorbate molecules. In the case of methanol reforming the phenomenon will not be an important consideration, unlike the position for the hydrogenation of the unsaturated hydrocarbons, where $R_{S_{max}}$ is greater than the smallest palladium crystallite radii which can be prepared in the unsupported state.

Catalyst Design

The wide variation in the value of N found in the palladium blacks after hydrogen pretreatment and the uncertainty in the value of d makes precise estimates of $R_{S_{max}}$ for other catalysts difficult. Nevertheless, it would not be unprofitable when designing a catalyst (particularly an unsupported one, but also a supported one), to use an average value of N (i.e. N=6) and approximate estimates of d, to predict the optimum particle size which will give the maximum specific surface area available for adsorption $(2R_{S_{max}})$ and thus maximum activity. There is no justification for decreasing ad infinitum the crystallite size of unsupported catalyst particles (16) in macroscopic aggregates without regard to this perhaps eventually having a detrimental effect upon the activity per unit weight of the catalyst.

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The Fabrication of Iridium Crucibles

DEEP DRAWING TECHNIQUES INVESTIGATED

Iridium has the greatest tensile strength of the platinum group metals and its melting point is 2443°C. Consequently, it has not proved to be an easy metal to fabricate in the past but efforts are continuing to improve the methods of working it. This technology has been stimulated by the increasing use of iridium in crucibles for growing single crystals from oxide melts (B. Cockayne, *Platinum Metals Rev.*, 1974, **18**, (3), 86–91).

A recent report from G. Reinacher of Degussa, Hanau (*Metall*, 1974, **28**, (7), 657–661) now shows that iridium can only be deep drawn satisfactorily to form seamless crucibles if the work on the iridium sheet is carried out above the recrystallisation temperature of the metal at ~1000°C. Tests included cupping from iridium discs 0.3 mm thick and 55 mm diameter, some being of cast iridium sheet and others of sintered iridium with and without ruthenium additions. The former for shaping the iridium was first heated to 620°C and later to 750°C. Variations in technique also included trials at pressures between 200 and 1000 kp, various widths of drawing gap, and intermediate annealing after the first 5.5–8 mm cupping. However, none of these techniques eliminated the formation of creases and the conclusion that working above ~1000°C is necessary was therefore reached.

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