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The Effect of Macroscopic Aggregation upon the Surface Area and Catalytic Activity of Palladium Blacks

P. A. SERMON

School of Chemistry, Brunel University, Uxbridge, England

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A theoretical model has been devised to account for and predict the effects of macroscopic aggregation of particles of unsupported catalysts and adsorbents. This shows that the fraction of the surface area which is available for adsorption diminishes as the number of inter-particular contacts increases, as the particle radius decreases, or as the size of the adsorbate molecule normal to the surface increases. The model allows the optimization of the crystallite sizes of unsupported catalysts to give maximum surface area available for a given set of adsorbates. A series of unsupported palladium samples, with crystallite sizes in the range 0.8 μm to 7 nm, have been used to study the phenomenon. Scanning electron microscopy indicates that, irrespective of differences in their size, the basic particles in each untreated sample are aggregated in very large open-structured ensembles. After some of the samples, which had been stored in air, were treated with hydrogen at 293 or 323 K, up to 64% of their surface areas were unavailable for the adsorption of 1-pentene or nitrogen. In the absence of sintering, this would result if the hydrogen–oxygen titration increased the degree of macroscopic aggregation until on average there were 12 inter-particular contacts per particle, i.e., the macroscopic aggregates were close-packed.

1. INTRODUCTION

When particles are not discrete, but in contact with one another, they exist in aggregates. Microscopic aggregates are the result of the clustering of atoms and these basic particles can further cluster into macroscopic aggregates.

Clearly, as microscopic aggregation proceeds the average particle size increases and this results in changes in the physical (*1*), sorptive (*2*) and catalytic (*3*) properties of the material. Despite extensive theoretical predictions (*4*) that macroscopic aggregation might affect physical adsorption and capillary condensation upon unsupported adsorbents, little experimental evidence has been published illustrating its effects. For example, differences in the surface area of a silica sample estimated by nitrogen (510 m^2 g^{-1}) and water (800 m^2 g^{-1}) adsorption which were claimed (*5*) to be the result of macroscopic aggregation, can also be explained in terms of micropores, produced during dehydration of a variety of materials, and which are therefore of such a size as to permit only the entry of the smaller water molecules (*6*). However, Wade (*7*) has studied the physical adsorption of nitrogen on alumina spheres, 7.5 nm in size, upon which water had been preadsorbed to varying extents and estimated the coordination number using the model of aggregation of Karnaukhov and Kiselev (*5*).

The effect of macroscopic aggregation upon chemisorption and catalysis has not been previously considered. This phenomenon and its effects have now been studied using unsupported palladium samples.

2. EXPERIMENTAL METHODS

Materials. Five palladium blacks, denoted A, B, C, D and E, were characterized

TABLE 1

THE SURFACE AREAS AND CRYSTALLITE/PARTICLE SIZES OF FIVE UNTREATED PALLADIUM BLACKS

	Sample	A	B	C	D	E
Surface area ($m^2 g^{-1}$)	Nitrogen BET 1			31.3_0	36.4_0	
	2				35.4_0	
	Krypton BET 1	3.5_4	7.1_5	30.8_1	36.7_6	66.0_7
	2	3.4_3	7.1_6	30.6_4	35.9_7	64.7_8
	Hydrogen chemisorption 1	3.6_3	7.4_1	32.7_0		71.8_6
	2					68.0_3
	3					71.7_1
	Av surface area	3.5_3	7.2_4	31.3_6	36.1_3	68.4_9
Particle or crystallite size (nm)	Electron microscopy	113	70	16		7
	X-Ray (spherical particles)	109	29	19		11
	(cubic particles)	88	23	15		9
	Calculated from av surface area assuming discrete uniform particles	141	69	16	14	7

for surface area and crystallite size by a number of techniques (*8*) and the results are shown in Table 1. A palladium sponge, previously (*9*) described as containing particles of 0.6 mm diameter, was also used. All samples were prepared by Johnson Matthey and Co. Ltd.

Methods. The sorptive and catalytic properties of the palladium blacks were investigated by adsorption of krypton and nitrogen at 77 K (*8*), hydrogen chemisorption at ambient temperature (*8*) and titration (*10*) of retained hydrogen with 1-pentene. In the alkene titration samples of the palladium blacks were reduced by hydrogen at 323 K, as described below; then, after flushing with nitrogen (30 cm^3 min^{-1}) for between 1 and 14 hr at 323 K, 1-pentene (161 ± 7 N m^{-2}) in nitrogen (101 kN m^{-2}, 10 cm^3 min^{-1}) was introduced to the blacks at 323 K. The products of the reaction were analyzed chromatographically with respect to time.

Macroscopic aggregates in the palladium blacks and sponge were observed using a scanning electron microscope (Stereoscan Instrument: S4: Cambridge Instruments Ltd.).

3. RESULTS

Theoretical model. Figure 1 shows a cross section through the simplest macroscopic aggregate, which consists of two particles of radius R, which are in contact at point X. Consider the adsorption of molecules of diameter (normal to the surface) d. This can only occur at points further from X than B, B', C and C'. Therefore the surfaces bounded by these points are not available for adsorption of such molecules. For each particle this unavailable surface area, S_{non}, is given by $S_{\text{non}} = 2\pi R^2 \int_{\phi_d}^{\phi_0} \sin \phi . d\phi = 2\pi R^2(1 - \cos \phi_d)$. Now, $\cos \phi_d = [R/(R + d)]$, and therefore $S_{\text{non}} = 2\pi R^2[d/(R + d)]$. This is equivalent to the approximate solution of Karnaukhov and Kiselev (*5*), $S_{\text{non}} = 2\pi R d$, making the assumption that R is very much greater than d. However, these authors associate d with the radius of the adsorbing molecule, rather than its diameter normal to the ad-

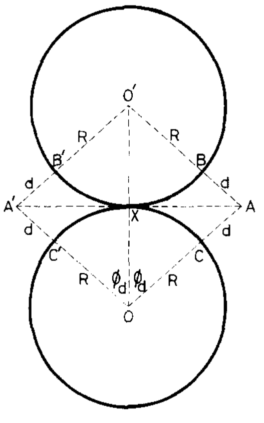

FIG. 1. A cross section through the simplest macroscopic aggregate.

sorbent surface. To convert this to an area which is not available per gram of sample, S_{non} must be multiplied by n, the number of basic particles per gram, where $n = (4/3\,\rho\pi R^3)^{-1}$ and ρ is the particle density.

For a sample containing these very simple macroscopic aggregates, the percentage surface area per particle which is unavailable for adsorption, $[(S_{\text{non}} \times 100)/S_{\text{total}}]$, is $100 \times [2\pi R^2 d/4\pi R^2(R + d)]$ or $50d/(R + d)$. This equals $50/(K + 1)$, where K is the ratio R/d.

In general, each basic particle will be in contact with N others, i.e., its coordination number is N, and the percentage loss in sample surface area per particle due to macroscopic aggregation is then given by $50N/(K + 1)$. Therefore the percentage of the surface area lost in this way increases as the value of N increases and the value of K decreases.

In these simplest macroscopic aggregates, adsorption can always occur at some value of ϕ, however large the value of d, but in aggregates exhibiting greater values of N this need not be so. If the basic particles are packed in a cubic array ($N = 6$) or are close-packed ($N = 12$) the maximum value of ϕ, $\phi_{\max}$, is only 45 or 30°, respectively. This means that adsorption can only occur if $\phi_d < \phi_{\max}$ or if K^{-1} ($= d/R$) is less than 0.414 or 0.155, respectively. In Fig. 2 the percentage of the surface area not available for adsorption is plotted against the average coordination number of the sample for various values of d/R. Since in the model ϕ_d can be greater than $\phi_{\max}$ at high values of N and d/R, the model can indicate that the percentage loss in surface area is greater than 100%. Provided macroscopic aggregation occurs with maximum angular separation between particles, the values of the percentage surface area unavailable for adsorption are valid below 100%, but have no significance above this value.

The model postulated here has the advantage over that previously published (5) in that it assumes no particular shape for the adsorbed molecules, but merely requires that ϕ_d is solely determined by d, the diameter of the adsorbed molecules in the direction normal to the adsorbent surface. However, restrictions upon the apparent overlap of molecules adsorbed along the circles generated by rotating BB' and CC' about OO' in Fig. 1 through 360° place constraints upon the model which are dependent upon their molecular shape. Spherical (diameter d) and conical (sitting upon the adsorbent at say B upon a base of

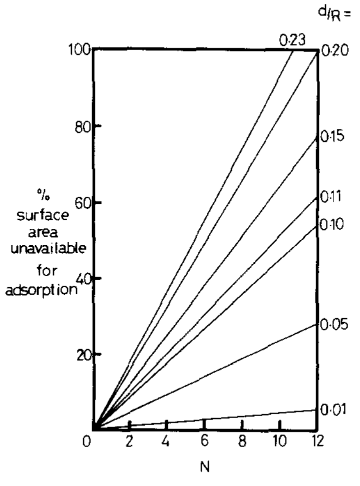

FIG. 2. The percentage surface area unavailable for adsorption plotted against N, coordination number, for various values of d/R.

diameter x and of height d with its apex at A) shapes are now considered for their simplicity and approximation to real adsorbed molecules (sphere: physically adsorbed inert gases, N_2, etc.; cone: linear ($d \gg x$) and aromatic ($d \ll x$) hydrocarbons.

For spherical molecules adsorbed along BB' and CC' in Fig. 1 the apparent overlap is at a maximum when the configuration of these spheres approximates to hexagonal close-packing and ϕ_d is 30°. Thus if the adsorbed molecules are spherical, the model is limited to adsorbate–adsorbent systems where, since $\cos \phi_d = R/(R + d)$, K^{-1} is less than 0.155. Alternatively, if a cone reasonably represents the adsorbed molecule, the model is applicable to systems exhibiting all values of K. Nevertheless, to avoid the overlap of molecules adsorbed along the circles on BB' and CC', the diameter of the cone base, x, must be less than $2R/(2K + 1)^{1/2}$. This condition approximates to $x < 2R$ as $K \rightarrow 0$ and the effects of aggregation become pronounced. Many adsorbates fulfil this requirement.

The systems studied here fulfil the above conditions of the model [assuming N_2 is spherical and 1-pentene is conical ($2R > x$)]. Other molecular shapes might be introduced into the model by invoking some ability of the molecules to be deformed and flexed. A previous model (*5*), assuming d to be the radius of spherical adsorbed molecules and not subject to restrictions on the apparent overlap of molecules adsorbed along the circles on BB' and CC', yields values of N which are about twice those estimated using the present model. However, as described below, the latter values approach the maximum ($N = 12$) themselves and thus the results of the present model are considered more realistic than those obtained by the previous model.

How well does this model represent real unsupported catalysts and adsorbents? Clearly, it is an approximate solution, since there are uncertainties in the value of d and it neglects the distribution of particle sizes ($2R$) and coordination numbers (N) in the sample, it assumes the basic particles to be spherical, neglects the effects of "menisci" (*11*) formed at the points of contact between particles and neglects any porosity of the basic particles. Therefore it is estimated that the uncertainty in the value of N estimated from experimental sorption data will normally be ±10%. Nevertheless, we now consider the validity of the model for some unsupported palladium samples of varying crystallite size.

Scanning electron microscopy. Transmission electron microscopy indicated (*8*) the presence of macroscopic aggregation in all of the untreated palladium blacks; indeed the phenomenon greatly hindered the application of the technique to the estimation of the size of the basic particles. The fact that the X-ray line-broadening of the palladium sponge (*12*) would be exhibited by crystallites very much smaller than 0.6 mm (*9*) indicates that macroscopic aggregation is also present in this sample.

Figure 3 shows a scanning electron micrograph of an untreated palladium black. In this, as in the other four blacks, macroscopic aggregates greater than 10 μm were observed, despite the wide variation in the size of the basic particles.

The absorption of hydrogen by these blacks at temperatures up to 333 K and the preceding hydrogen pretreatment at ambient temperature were found (*8*) to cause no sintering, no increase in size and no change in shape of the basic particles. However, this sorption procedure caused the samples used to form a single aggregate, which like the original aggregates, (see Fig. 3) could be easily broken by ultrasonic waves (*8*) or mechanically. This indicates that the bonds between particles can be produced at temperatures generated during hydrogen absorption or pretreatment, i.e., hydrogen–oxygen titration, but

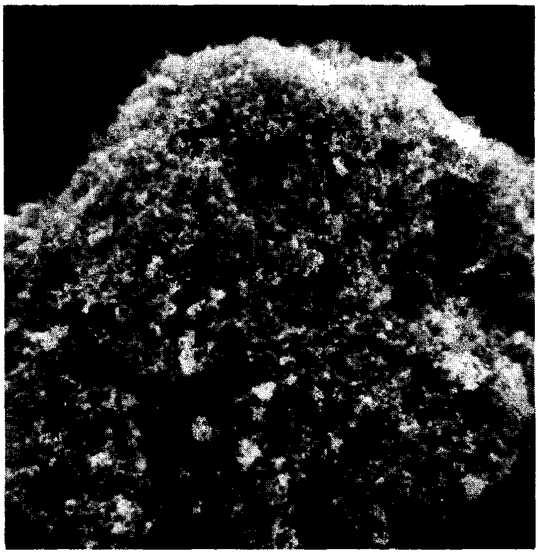

FIG. 3. Scanning electron micrograph of an untreated palladium black sample: sample A × 8510.

that they possess no great strength. This same phenomenon was observed after the hydrogen pretreatment and alkene titration to be described later. As an example, Fig. 4a and b show scanning electron micrographs of sample C after this hydrogen pretreatment and titration with 1-pentene at 323 K. Unfortunately, removal from the reactor involved breakage of the single aggregate (6 × 6 mm × 1 cm) but nevertheless a fragment which is 3 mm in diameter can be observed. This must consist of up to about 10^7 of the smaller macroscopic aggregates illustrated in Fig. 3 and noted in all untreated black samples. Figure 4b shows the open structure of this aggregate.

Figure 4c and d are scanning electron micrographs of an aggregate of the palladium sponge. Despite its treatment at up to 590 K in hydrogen (*9*, *12*) one can see that the macroscopic aggregate in Fig. 4c, which is approximately 0.1 mm in diameter, consists of basic particles, which are 0.2 to 0.8 μm in diameter. Therefore, unlike aggregates later found to exhibit high values of N, these aggregates, in which the value of N appears to be low, are open-structured ensembles of relatively small basic particles.

Alkene titration. The theoretical model for macroscopic aggregation predicts that the phenomenon causes the percentage of the surface area of basic particles not available for adsorption to increase as the coordination number N increases, R decreases or d increases. Hence one would expect the phenomenon to affect the adsorptive and catalytic behavior of some of these palladium samples in the titration of retained hydrogen with 1-pentene.

This alkene titration has been shown (*10*) to be a valuable technique for estimating the surface area of silica-supported platinum and Fig. 5 shows the general form of a plot for the titration of prereduced Pt/SiO_2 with 1-pentene at 373 K. Areas I and II were assumed to be associated with titration of platinum-held hydrogen and silica-held or "spilt-over" (*13*) hydrogen, the latter being assumed to migrate slowly back to the platinum for titration by 1-pentene. Platinum crystallite sizes calculated from area I were in good agreement with estimates by other techniques (*10*,*13*). Thus for these unsupported palladium samples, in the absence of macroscopic aggregation and absorbed hydrogen (*8*,*14*), one might expect to observe

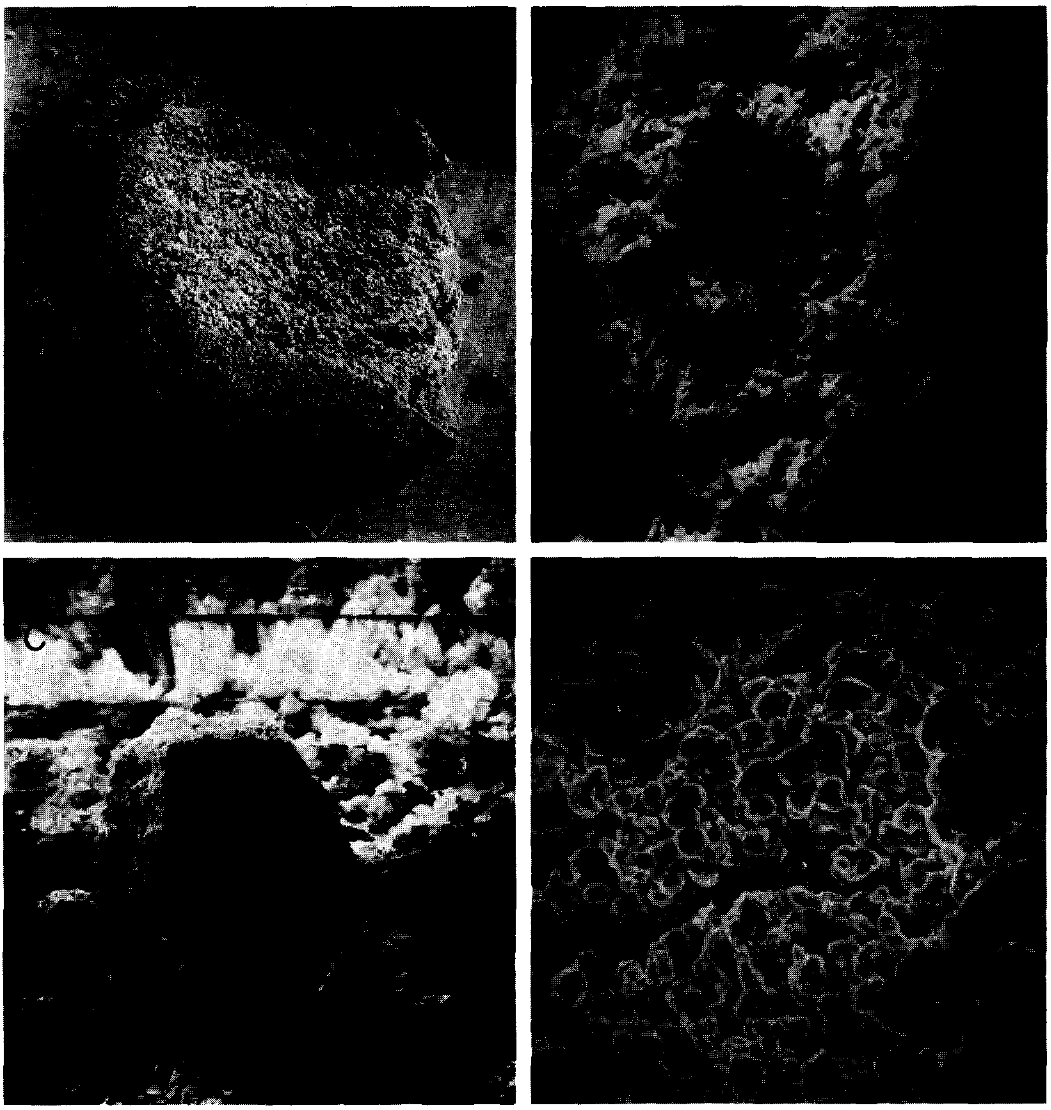

FIG. 4. Scanning electron micrographs of macroscopic aggregates in sample C: (a) × 50 (some fibers of Pyrex have also been bound into the aggregate); (b) × 6000 after hydrogen treatment and titration with 1-pentene at 323 K, and in a palladium sponge (c) × 321; (d) × 8740 after hydrogen treatment and absorption of hydrogen at up to 590 K.

only area I. Now, by virtue of the difference in the size of hydrogen atoms and 1-pentene molecules, the former will have access to all of the palladium surface, but macroscopic aggregation may make a fraction of the surface unavailable to 1-pentene adsorption. Where this occurred the plots would exhibit tails (areas II) and the area I would be reduced, provided the rate of migration of hydrogen across the palladium surface from regions unavailable to 1-pentene was slower than the maximum rate of titration of hydrogen by 1-pentene (8×10^{17} atoms min^{-1} under experimental conditions) and that absorbed hydrogen was absent.

After pretreating the samples A, B, C and E at 323 K with hydrogen (30

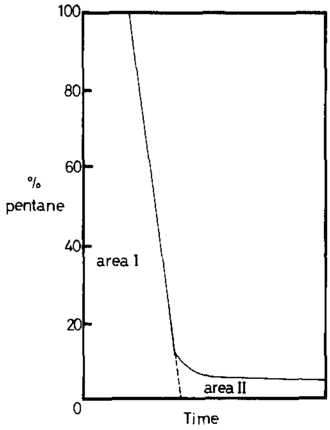

FIG. 5. A typical plot obtained for the titration of hydrogen adsorbed on Pt/SiO_2 by 1-pentene at 373 K.

$cm^3 min^{-1}$, 101 kN m^{-2}) for 1 hr, they were flushed with pure nitrogen (30 cm^3 min^{-1}, 101 kN m^{-2}) for 1 hr at the same temperature. The samples were then titrated with 1-pentene (161 ± 7 N m^{-2}) in nitrogen (10 cm^3 min^{-1}, 101 kN m^{-2}). Assuming one hydrogen was adsorbed by each surface palladium atom (*8*, *14*) and that 1.2×10^{19} palladium atoms exist per square meter of surface (*15*), the specific surface areas of the samples were calculated from the total number of titrated hydrogen atoms. These values were far in excess of the surface areas indicated in Table 1, which means that some absorbed hydrogen must have remained despite the nitrogen flushing. The calculated values of H/Pd, the ratio of number of sorbed hydrogen atoms to the total number of palladium atoms, were 0.0459(A), 0.0874(B), 0.1864(C) and 0.1634(E), which are 5.7(A), 5.5(B), 2.7(C) and 1.1(E) times greater than the values found (*8*) when only adsorbed hydrogen is titrated. Therefore it was only with sample E, containing the smallest crystallites, that agreement was reasonable and that absorbed hydrogen might have been absent. This effect of particle size upon the rate of hydrogen desorption is to be expected. Further, if sample A was flushed with pure nitrogen (10 cm^3 min^{-1}, 101 kN m^{-2}) for 14 hr the value of H/Pd found only fell to 0.0317, which is still four times greater than that for adsorbed hydrogen alone. Thus at 323 K it appears that hydrogen absorbed by palladium, with crystallites between 141 and 7 nm in size, cannot be removed simply by flushing with nitrogen at atmospheric pressure over long periods of time, despite the fact that it can readily be removed under vacuum treatment at much lower temperatures (*8*, *14*, *16*). This was confirmed by the inapplicability of the titration technique to the estimation of the surface area of palladium supported on silica (*10*) after a similar nitrogen flushing. This observation has important implications for the study of the interaction of hydrogen with palladium by chromatographic techniques (*17*) which normally employ this type of flushing, since the tenacity of absorbed hydrogen under these conditions has not been recognized previously.

In an effort to eliminate the complication of absorbed hydrogen, a new pretreatment of the samples A, B, C, D and E consisted of flushing with nitrogen (30 cm^3 min^{-1}, 101 kN m^{-2}) for 1 hr at 323 K, flushing with a mixture of hydrogen (0.67 kN m^{-2}) and nitrogen (100.41 kN m^{-2}) at 30 cm^3 min^{-1} for 1 hr at 323 K, and flushing with pure nitrogen (30 cm^3 min^{-1}, 101 kN m^{-2}) for 2 hr at 323 K. Such a low partial pressure of hydrogen should minimize absorption of hydrogen and it has been shown (*8*, *14*) that, provided the α–β phase transformation does not occur, desorption of any absorbed hydrogen is facilitated. The titration with 1-pentene in nitrogen was then carried out at 323 K and the titration plots shown in Fig. 6 were obtained. The good agreement between the titration plots of different runs on each sample indicates the excellent reproducibility of the technique.

One would expect the effects of macroscopic aggregation to increase as *R* decreases, i.e., as we proceed from samples A to B to C to D to E. The total

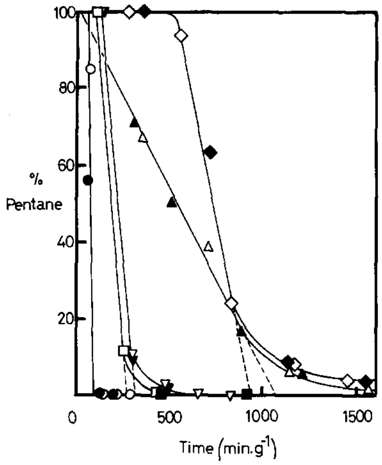

FIG. 6. Plots obtained for the titration of hydrogen held on palladium black samples: A (○,●); B (▽,▼); C (△,▲); D (□,■); E (◇,◆) by 1-pentene at 323 K. Black symbols denote repeat runs.

surface area, the surface area available for 1-pentene adsorption and the surface area not available for 1-pentene adsorption were calculated for each palladium black from the total number of hydrogen atoms titrated and the number of hydrogen atoms titrated in areas I and II of their plots in Fig. 6. These surface areas are plotted against the average area estimated by other techniques (see Table 1) in Fig. 7.

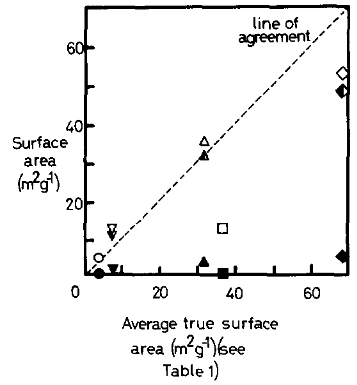

FIG. 7. Comparison of the total surface areas of palladium black samples: A (○), B (▽), C (△), D (□), E (◇) with those estimated by alkene titration (open symbols, total surface area; half-filled symbols, surface areas available to 1-pentene adsorption; black symbols, surface area unavailable for 1-pentene adsorption).

The agreement between the values of total surface area is reasonable for all samples, except D and E, where the estimate of the 1-pentene titration is 64 and 22% lower than the average estimate of the other techniques, which are not severely complicated by the effects of macroscopic aggregation (note agreement between areas determined with adsorbates of different size in Table 1). Similarly for these two samples the surface area available for the adsorption of 1-pentene is only 35 and 70% of the total area estimated by these other techniques. Since these samples contain the smallest palladium crystallites, one would expect the effects of macroscopic aggregation to be most pronounced for them.

Unfortunately, there is no information published on the thickness of chemisorbed monolayers on metals. However, one can calculate an approximate value for the volume occupied by a chemisorbed molecule of 1-pentene, $[M/(\rho \times 6.0235 \times 10^{23})]$, where the molecular weight, M, is 70.13 and the liquid density, ρ, is 0.6411×10^{-21} g nm^{-3} at 295 K (*18*), to be 0.185 nm^{-3}. If it is assumed that 1-pentene is chemisorbed as shown in Fig. 8, then d/x is 0.85 and, correcting for its surface mobility by allowing rotation about OO', the surface area it occupies is $\pi(x/2)^2$. In this conical configuration $\frac{1}{3}\pi(x/2)^2(0.85x)$ equals 0.185 nm^3 and d is 0.799 nm. Thus the values of d/R (or K^{-1}) for samples A, B, C, D and E are, taking R as half the average crystallite diameters in Table 1, 0.011, 0.023, 0.100, 0.114 and 0.228. This means that the percentages of the surface area which were found to be unavailable for the adsorption of 1-pentene, i.e., 65% (sample D) and 30% (Sample E), would be caused by an average coordination number, N, of about 12 (12.7 ± 1.3) and 3 (3.2 ± 0.3), respectively (see Fig. 2). If 3 were also the average coordination number for the aggregates in samples A, B and C, then the available surface areas would be

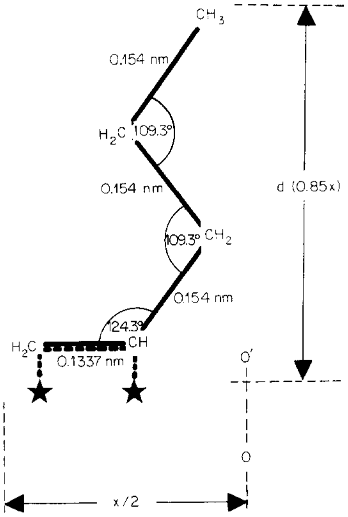

FIG. 8. The configuration assumed for adsorbed 1-pentene [(★) a surface palladium atom] using bond lengths and angles from Ref. (*18*).

more than 90% of the total surface areas and such differences are not detected. A value of 3 for the coordination number, *N*, is in agreement with previous estimates (*7*) and appears to be consistent with the fact that in Fig. 4d it can be judged qualitatively that in aggregates of the palladium sponge *N* has neither a very high ($N = 12$) nor very low ($N = 1$) value. However, the value of 12 for sample D is the maximum possible and corresponds to close-packing of the basic particles. It is evident that *N* is not solely dependent upon the size of the basic particles in an aggregate, but is affected by other factors such as the exact details of its preparation and subsequent treatment by hydrogen. It is possible that the different titration slope exhibited by palladium black C (see Fig. 6) is the result of a wide distribution of *R* or *N* in this sample.

How then are the catalytic properties of these palladium black samples affected by this macroscopic aggregation? In agreement with previous results for silica-supported palladium and platinum (*10*), it was found (see Fig. 9) that, as the titration of adsorbed hydrogen by 1-pentene proceeds and the adsorbed hydrogen concentration decreases, the predominant products are first *n*-pentane, then *trans*-2-pentene and *cis*-2-pentene, and finally 1-pentene itself. However, it was only with samples A (low degree of aggregation), C (low degree of aggregation) and D (high degree of aggregation) that the percentage *n*-pentane produced, which is a measure of the availability of adsorbed hydrogen, fell to below about 0.01 to 0.02% and 1-pentene was observed as the final predominant product (see Fig. 6). In the case of other samples, the titration was not continued long enough for the hydrogen on the samples to become so depleted that the isomerization ceased.

Therefore there is no relationship between particle size or the degree of macroscopic aggregation and ability to isomerize/hydrogenate alkenes. Indeed, the only effect of macroscopic aggregation upon the catalytic properties of these palladium blacks must be a diminution of the specific surface area available for adsorption as *N* increase, *R* decreases or *d* increases. This would therefore be accompanied by a loss in activity per unit weight of catalyst.

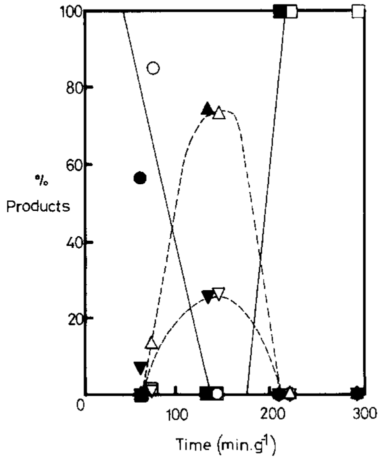

FIG. 9. The complete distribution of products: *n*-pentane (○,●); *trans*-2-pentene (△,▲) *cis*-2-pentene (▽,▼); 1-pentene (□,■) during the titration of hydrogen adsorbed on sample A by 1-pentene at 323 K. Black symbols denote points on a repeat titration run.

It is interesting to speculate that differences in the abilities of palladium and platinum to isomerize alkenes (*19*), the former showing the more marked tendency to isomerize, might be explained by the tenacity of absorbed hydrogen in palladium under conventional conditions for testing catalysts, i.e., at relatively high pressure. This absorbed hydrogen in palladium could be generated during the reduction of the catalyst and could then slowly migrate back to the palladium surface to sustain the concentration of adsorbed hydrogen at a sufficient level to permit the continuation of isomerization.

Adsorption results. For all of the untreated palladium black samples the surface areas determined by nitrogen or krypton adsorption at 77 K are in very good agreement with those estimated by hydrogen chemisorption (see Table 1). However, the value of d for physically adsorbed nitrogen has been calculated to be 0.43 nm (*20*), which would mean that if N were 12 in samples D and E, then 29 and 55% of their surfaces would be unavailable for adsorption by nitrogen. Therefore, from the data in Table 1 it must be inferred that virtually all of the surface of each sample is available for adsorption by hydrogen, krypton or nitrogen, and hence that aggregation has no effect upon such adsorption. Thus the value of N must be low in each untreated sample. Now we have seen, using the alkene titration, that in samples D and E macroscopic aggregation does affect their sorptive properties after hydrogen treatment at 323 K. Indeed this treatment causes the formation of single macroscopic aggregates.

Confirmatory evidence for the fact that it is the treatment of the oxide surface on the palladium blacks with hydrogen at low temperatures which causes significant increases in the value of N in the macroscopic aggregates can be seen in Table 2. The surface area of sample E, which had an original average value of 68.4_9 m^2 g^{-1} (see Table 1), has been estimated by the adsorption of hydrogen, nitrogen and krypton, after hydrogen pretreatment at 293 K to remove the surface oxide layer and heating it to 363 K in hydrogen, using various subsequent treatments. First, although there has been some slight sintering caused by heating the sample to 363 K in hydrogen (*8*), no further sintering occurred during the measurement of the sequence of results denoted 1, 2 and 3 in Table 2. The surface area of the sample

TABLE 2

THE SURFACE AREA OF SAMPLE E DETERMINED AFTER HYDROGEN TREATMENT [H–O TITRATION (5)] AT 293 K AND HEATING IN HYDROGEN TO 363 K, USING VARIOUS SUBSEQUENT TREATMENTS

Measurement no.	Method	Immediate sample pretreatment	State of surface	Specific surface area (m^2 g^{-1})
1	Hydrogen chemisorption (273 K)	H_2 (343 K)	H–Pd	57.7_0
2	Nitrogen BET (77 K)	H_2 (343 K) + evacuation	H–Pd	21.3_5
3	Hydrogen chemisorption (273 K)	Evacuation + H_2 (273 K)	H–Pd	58.1_9
4	Nitrogen BET (77 K)	air (293 K) + evacuation	O–Pd	12.7_0
5	Krypton BET (77 K)		O–Pd	16.8_7
6	Krypton BET (77 K)		O–Pd	17.2_9
7	Krypton BET (77 K)		O–Pd	17.2_8
8	Krypton BET (77 K)		O–Pd	16.1_5

after hydrogen titration of its oxidized surface (surface: Pd–H) measured by hydrogen chemisorption is 57.9_5 m^2 g^{-1} (average of measurements 1 and 3) but by nitrogen adsorption is 21.3_5 (measurement 2). It is known that under these conditions the surface area is stable and no sintering occurs (*8*). Therefore if we assume that these differences in surface areas are the result of macroscopic aggregation caused during the first hydrogen pretreatment at 293 K and that hydrogen chemisorption, because of the relatively small size of the adsorbed species, measures the total surface area, then for this sample (Sample E) 63% of the total surface area is unavailable for the adsorption of nitrogen or krypton. Now taking the value of d/R (or K^{-1}) as 0.123 for the adsorption of nitrogen upon sample E, then, within the errors set by the uncertainty in the value of d, etc., this loss in the available surface area would be caused by macroscopic aggregation involving a value of N of 11.5 ± 1.2. This maximum value of N is similar to that detected in sample D, the second highest surface area sample, by alkene titration.

After the treatment of the reduced black with oxygen at 293 K, nitrogen and krypton adsorption indicate (measurements 4–8 in Table 2) a much lower surface area than nitrogen adsorption on the reduced material. It is unlikely that this could be the effect of preadsorbed oxygen and hydrogen (*21*) and it appears that this oxygen treatment of the reduced surface at 293 K (oxygen–hydrogen titration) causes microscopic aggregation or sintering in the sample, unlike the reverse titration.

4. CONCLUSIONS

Macroscopic aggregation has been found in six untreated palladium blacks, which have particle sizes in the range 0.8 μm to 7 nm. These aggregates have been shown to be relatively large openstructured ensembles, containing more particles than the aggregates previously studied (*22*). Nitrogen and krypton adsorption at 77 K on untreated palladium blacks suggests that the coordination number in these aggregates is very low. However, hydrogen treatment (hydrogen–oxygen titration) of the catalysts at or close to ambient temperature caused all of the blacks to form single macroscopic aggregates. The theoretical model of macroscopic aggregation indicates that the fraction of the surface area of the hydrogen treated blacks which is found to be unavailable to adsorption of 1-pentene and nitrogen or krypton could be caused by average coordination numbers of 12 [i.e. $(11.5 + 12.7)/2$] in samples D and E. Now, although these are the catalysts containing the smallest palladium crystallites (see Table 1) their coordination numbers were not simply dependent upon the size of the basic particles and indeed at present they could not easily be reproduced (hydrogen treatment of sample E gave $N = 3$ (alkene titration) and $N = 12$ (nitrogen adsorption) on different occasions). Nevertheless, it is clear that hydrogen treatment (or hydrogen–oxygen titration) upon palladium blacks at ambient temperature can induce a remarkable increase in the extent and ordering of macroscopic aggregation. It may be that temperatures produced on the surface of catalyst particles is sufficient to facilitate inter-particle chemical bonding and meniscus formation [see Fig. 1b in part II of Ref. (*9*) and Ref. (*11*)]. Further investigation is required to discern other factors affecting this phenomenon.

What are the effects of macroscopic aggregation on the sorptive and catalytic properties of unsupported materials predicted by the model suggested here? In Fig. 10 we plot the specific surface area of palladium, $(12\pi R^2 - S_{\text{non}} \cdot N)/(4\rho\pi R^3)$, where ρ is the particle density (12.02×10^{-24} g nm^{-3}), as a function of R for various values of d, assuming N has a value of 12. It is normally assumed that, in

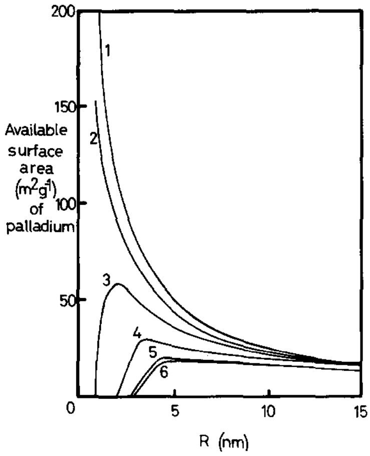

FIG. 10. The specific surface area of unsupported palladium, which is available for adsorption by molecules of length normal to the surface d [assuming N is zero (1) or N is 12; (2) $d = 0.07$ nm; (3) $d = 0.2$ nm; (4) $d = 0.4$ nm; (5) $d = 0.57$ nm; (6) $d = 0.6$ nm] plotted against R.

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 specific activity of the catalyst. However, as shown in Fig. 10, the available surface area goes through a maximum at $R_{s\ max}$ determined by the size of the adsorbate molecule. If R is greater than $R_{s\ max}$, then the specific surface area does indeed increase with decreasing R, but if R is less than $R_{s\ max}$, the opposite effect is observed. A similar set of curves can be drawn for each value of N chosen and in Fig. 11 the values of $R_{s\ max}$ are plotted against the corresponding values of d when N equals 4, 8 and 12. Thus, if a palladium black is required to hydrogenate 1-pentene, to decrease its particle diameter below 14 nm (N = 12), 10 nm (N = 8) or 4 nm (N = 4) has an adverse effect upon the effective specific surface area available for adsorption of the alkene, and hence the activity per unit weight of catalyst. Let us consider two more examples. In Fig. 10 it can be seen that it would be disadvantageous to decrease the diameter of particles in a palladium black used in the hydrogenation of stilbene in the liquid-phase (*22*), for which d is calculated in an analogous manner to that used for 1-pentene to have a value of 0.57 nm, below 9 nm (N = 12). However, if the black is required as an electrocatalyst for the reforming of methanol in a fuel-cell (*24*), for which d is calculated in an analogous manner to that used for 1-pentene to have a value of 0.07 nm, $R_{s\ max}$ is less than 1 nm (N = 12) and therefore below the usual particle size found for palladium blacks. We have seen the wide variation in the value of N exhibited by palladium blacks and this, together with the possible errors in the estimated values of d, means that it is not profitable to estimate the values of $R_{s\ max}$ for real catalysts unless these parameters are precisely known. However, the fact that the value of d for chemisorbed ethylene may be about 0.5 nm, i.e., the thickness suggested for hydrocarbons adsorbed parallel to a Graphon surface (*25*), means that the effects of macroscopic aggregation might be observed in the catalyzed reactions of this and higher hydrocarbons. It follows that it is important to compare the activities of materials exhibiting macroscopic aggregation on the basis of the area available for adsorption rather than the total surface area, since the phenomenon will cause the differences in activity per unit weight to be underestimated.

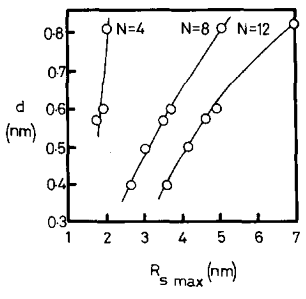

FIG. 11. The variation of R at the maximum surface area, $R_{s\ max}$, with the thickness of the chemisorbed layer, d, for coordination numbers of 4, 8 and 12 within the macroscopic aggregates.

It is clear that techniques used to characterize the size of particles in unsupported materials must be capable of differentiating between basic particles and macroscopic aggregates. X-Ray line-broadening, electron microscopy and gas adsorption, using suitable adsorbates, have been found (*8*) to be suitable methods.

Although macroscopic aggregation is most prevalent in unsupported materials, it has also been noted in supported adsorbents and catalysts (*26*). The theoretical model postulated here to describe the effects of macroscopic aggregation observed for unsupported palladium blacks is applicable to any system where the phenomenon exists.

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