The Structure and Activity of Supported Metal Catalysts

VIII. Chemisorption and Benzene Hydrogenation on Palladium/Silica Catalysts

R. L. Moss, D. Pope, B. J. Davis, and D. H. Edwards

Warren Spring Laboratory, Stevenage, Hertfordshire, England

The chemisorption of CO and H_2 on two series of Pd/silica catalysts, reduced at 300 or 450°C and containing 0.5 to 25.0% Pd, was measured. Palladium areas were calculated on the basis of different assumptions about the crystal planes exposed and the stoichiometry of CO and H_2 adsorption on Pd, and compared. X-ray line-broadening measurements of crystallite size provided some confirmation of the assumptions made in determining Pd areas by chemisorption. Electron micrographs of thin catalyst sections provided direct evidence of crystallite sintering or aggregation in catalysts with the higher Pd loadings. It was concluded that increasing Pd content only increased the crystallite size, but not apparently the distribution of exposed planes. Specific activity for benzene hydrogenation at 100°C was independent of crystallite size for both series of catalysts within the size ranges 13 to 114 and 16 to 134 Å. The possibilities for observing crystallite size effects are discussed. Specific activity decreased with increasing reduction temperature; the effect was observed using different silica supports, Pd salts, and Pd contents. Specific activity also varied for catalysts prepared on different silicas but with a fixed reduction temperature and Pd content. Various explanations of the effect of reduction on specific activity are considered including the interaction of palladium and silica which certainly occurred when the reduction temperature was raised to 600°C.

INTRODUCTION

Benzene hydrogenation in the gas phase has been used as the test reaction in a number of previous studies of structure-sensitivity in catalyzed reactions. Dorling and Moss (1) found constant specific activity for a range of platinum dispersions on silica. Subsequently, it was shown that specific activity was independent of platinum crystallite size in the range 10 to 50 Å (2, 3), the nature of the support [silica or alumina (2)], or choice of platinum complex used in catalyst preparation (3). Hence, if the surface structure had changed in the way suggested by models of perfect crystallites below 70-Å size, or had other-

wise varied with catalyst preparation, benzene hydrogenation over platinum would be a structure-insensitive reaction. However, ultradispersed platinum (< 10-Å size) appears to be less active than expected (4). For benzene hydrogenation over supported nickel, the earliest studies found that small crystallites had either a lower or higher specific activity than larger nickel crystallites, but a number of subsequent publications reported approximately constant specific activity despite changes in nickel content (5, 6) or degree of sintering (2). In more recent work (7) maximum specific activity was observed in nickel/silica catalysts containing nickel crystallites

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of 12-Å mean size. The choice of support had either no effect (2) on specific activity or some effect, especially at low nickel contents (8).

For the third metal of importance in catalytic hydrogenation, palladium, much less is known about possible influences on the specific activity due to variation in crystallite size and other preparative variables. Aben et al. (2) found constant specific activity for benzene hydrogenation over palladium supported on silica or alumina, where the palladium dispersion was varied by sintering in hydrogen. In the present work on palladium/silica, the dispersion was varied by changing the palladium content and the catalysts were reduced at one of two fixed temperatures (thereby providing two series of catalysts). Reduction temperature, silica area, and the palladium compound used in catalyst preparation, were also separately investigated, with respect to possible effects on the specific activity of these catalysts for benzene hydrogenation.

In all such studies of structure-sensitivity in supported metal catalysts, the actual changes induced in the surface structure of the crystallites remain largely unproven. Now, there is evidence (9) that the maximum density of CO molecules adsorbed (under defined conditions) on each of the major low index planes only varies moderately, whereas the number of chemisorbed hydrogen atoms is assumed to be closely related to the number of exposed surface atoms. Therefore, in the present work an attempt has been made to detect change in the distribution of the surface planes (as the palladium content is increased) by careful comparison of the hydrogen and CO chemisorption data.

EXPERIMENTAL METHODS

Catalyst preparation. Unless otherwise stated, catalysts with 0.5 to 25% Pd were prepared from appropriate strength solutions of tetraamminepalladous nitrate (Johnson Matthey "Specpure"). Hence in each preparation the silica gel (usually Davison grade 70) could be wetted with just sufficient solution, evaporated to dryness with stirring on a water bath, and then dried overnight in an air oven at 100°C. Higher temperatures decomposed the palladium salt prematurely. Catalysts were reduced at temperatures specified later by first purging a small sample with helium (before chemisorption measurements) or nitrogen (before benzene hydrogenation) then raising them to the specified temperature, usually 300 or 450°C, in hydrogen (50 ml/min, purified by passage through a heated palladium–silver thimble). Other silicas sometimes used were a series of "Porasil" chromatographic column supports (Pechiney–Saint–Gobain, from Waters Associates), Cab-O-Sil HS-5 (Cabot), and Sorbsil ID No. 1 (Crosfields).

Chemisorption measurements. A description of the equipment has already been published (10). The sample weight (0.3 to 0.8 g) was chosen depending on Pd loading to facilitate accurate measurement of the gas uptake. The sample was maintained at 33°C, the equilibrium time was usually 3 min, and the isotherms were measured over the range 0 to 10 Torr. In experiments where both hydrogen and CO chemisorption were to be studied, the sample, after reduction for 2 hr, was outgassed overnight at the same temperature, and a helium dead-space was determined, evacuated, hydrogen chemisorbed, and outgassed for 2 hr (again at the initial reduction temperature), and then CO was chemisorbed. The reverse procedure, where CO was chemisorbed before hydrogen, was found to be unsatisfactory. Volumes adsorbed were related to the sample weight after discharge. Samples used in benzene hydrogenation tests were subjected to the same reduction (at 300 or 450°C) and outgassing procedures before determining their palladium areas.

TABLE 1

Chemisorption and X-ray Data

Reduction temperature (°C)	Pd content (%)	Pd surface areas		Crystallite size (Å)
		S_{CO} (m²/g cat.)	S_{H_2} (m²/g cat.)	
300 (in situ)	0.5	0.55	1.00	
	1.0	0.73	1.19	
	2.5	3.75	2.64	
	5.0	4.71	5.10	
	8.0	4.40	4.29	
	10.0	5.02	5.76	
	15.0	5.82	—	
	25.0	7.21	9.48	
450 (in situ)	0.5	0.44	0.65	—
	1.0	1.40	1.57	54
	2.5	2.75	—	—
	5.0	3.27	3.73	83
	8.0	—	2.81	152
	10.0	4.41	4.81	117
	15.0	5.68	6.40	162
	25.0	7.80	8.46	156
450 (external)	5.0	3.54	3.83	
	10.0	3.83	4.17	
	15.0	4.27	5.44	
	25.0	5.31	7.82	

Instrumental methods. Catalysts were examined by electron microscopy in the form of thin sections cut on an ultramicrotome. The sample was prepared for cutting by setting in a block of "Araldite" resin. Details of the procedure are given in Ref. (*10*). The electron microscope used had a rated best-line resolution of 4.5 Å, and the point resolution for these samples was about 10 Å. Crystallite sizes were determined by X-ray line-broadening using a procedure similar to that previously described (*11*), except that integral peak breadths were used. The account of X-ray line-broadening applied to supported metal catalysts given in Ref. (*10*) is the relevant background to the methods used in the present work.

Catalytic activity tests. Benzene hydrogenation rates were measured in an atmospheric pressure flow system incorporating a narrow U-tube glass reactor (6-mm o.d.) fitted with a side-arm for the exit gas so that a thermocouple, through a glass joint, could be inserted directly into the small bed of catalyst (~0.25 g). Benzene was picked up from a saturator, cooled to 6°C (by external refrigerant circulation) using a small flow of pure hydrogen, and then diluted with further pure hydrogen (from a diffusion unit) to give a flow rate of 120 ml min⁻¹, containing 1.92% benzene. Before testing, the catalyst sample was purged and then reduced with purified hydrogen for 16 hr, usually at 300 or 450°C. Measurements were made at a series of fixed temperatures from ambient upward, analyzing the reactants and products chromatographically. Arrhenius plots of the data were made from which conversions at the chosen comparison temperature, 100°C, were obtained.
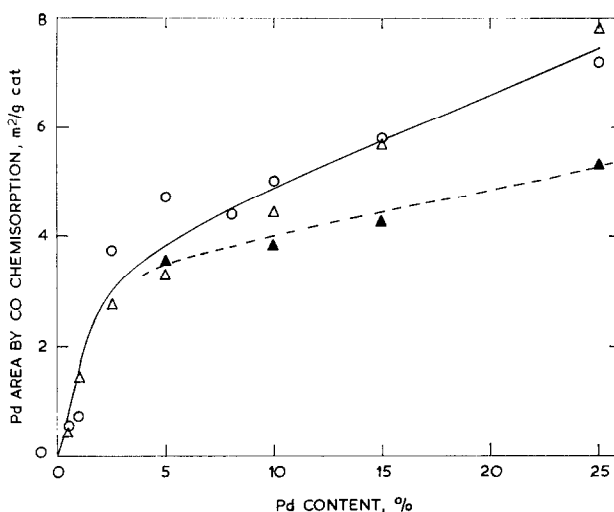
FIG. 1. Palladium areas from CO chemisorption as a function of Pd content: catalysts reduced *in situ* at 300 (○) or 450°C (△); catalysts reduced externally at 450°C and re-reduced before CO adsorption (▲).

RESULTS AND DISCUSSION

Carbon Monoxide Chemisorption

Table 1 shows the Pd surface area derived from CO chemisorption measurements as a function of the Pd content of the catalysts, which had either been reduced at 300 or 450°C *in situ*, or reduced externally at 450°C, then transferred and re-reduced in the chemisorption apparatus at the same temperature. In calculating the Pd area from the CO adsorption isotherm at apparent saturation coverage, it was assumed that 0.84×10^{15} CO molecules occupied each square centimeter of Pd surface. This value was taken from LEED work (9) with single crystal planes of palladium which showed that the maximum density of adsorbed CO molecules [room temperature; $P_{CO} \leqslant 10^{-4}$ Torr (1 Torr $= 133.3$ N m^{-2})], as derived from structure models, varied little [0.77, ~0.80, and 0.94×10^{15} cm^{-2} for the (111), (100), and (110) planes] despite the three-fold variation in the density of surface atoms. At low and medium coverage, the adsorbed species are located at highly symmetrical adsorption sites, whereas maximum coverage is

characterized by a tendency to form close-packed adsorbate layers.

The calculated adsorption stoichiometry Pd$_s$/CO, i.e., the ratio Pd(surface)/CO adsorbed, had values of 2.0, ~1.7, and 1.0 for the (111), (100), and (110) planes, respectively. The density of adsorbed molecules used here to calculate the Pd surface area, i.e., 0.84×10^{15} cm^{-2}, is the mean CO adsorption value for the three main low-index planes (mean density, 1.27×10^{15} Pd atoms cm^{-2}) and yields a Pd$_s$/CO ratio of 1.5. Values of Pd$_s$/CO arising in work with a variety of supported palladium catalysts are summarized in Table IV of Ref. (10), and vary between 1 and 2. Such variation seems possible as a consequence of the palladium crystallites in the catalysts examined exposing a different "mix" of surface planes. However, in the preliminary presentation of CO chemisorption data shown as Fig. 1, it is assumed that the "mix" of surface planes did not vary with increasing Pd content.

Catalysts with the same Pd content have similar palladium surface areas whether reduced *in situ* at 300 or 450°C (unbroken
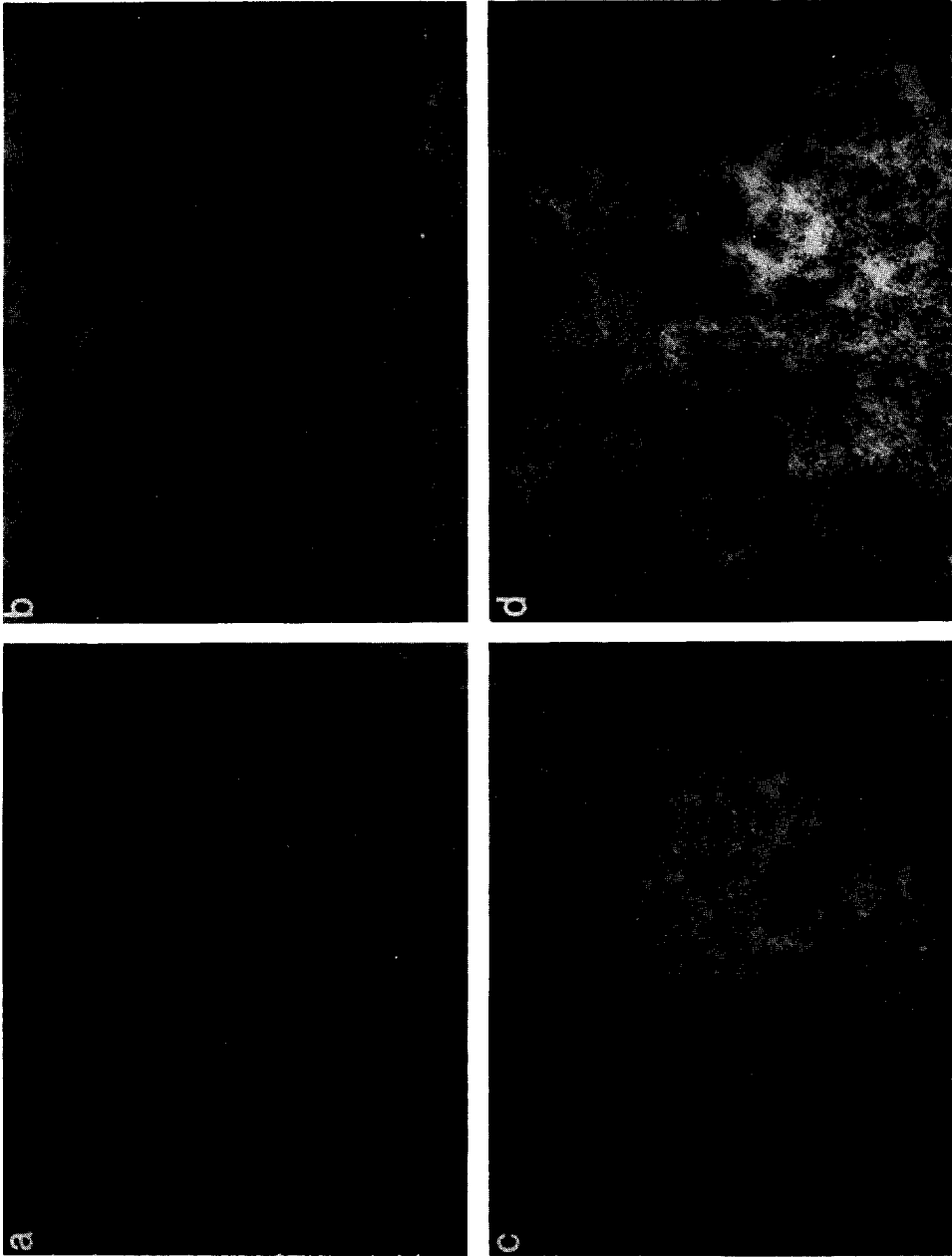
FIG. 2. Electron micrographs of ultramicrotome sections: 5% Pd/silica reduced at (a) 300 and (b) 450°C; 10% Pd/silica reduced at (c) 300 or (d) 450°C. Magnification, × 60,000.

curve, Fig. 1). At low metal loadings, the Pd area increased sharply with increasing Pd content, but above 3% Pd the slow growth in area suggests extensive sintering or crystallite aggregation. A model for crystallite formation in supported metal catalysts prepared by (genuine) impregnation, where there is no interaction between the metal salt and the support, has been described previously (*12*). It predicts that initially an increase in metal loading nucleates more crystallites and the metal area is approximately proportional to metal content. At higher metal loadings, the crystallites will remain constant in number (consistent with the number of pores in the support) but increase in size so that the metal area will be proportional to (metal content)$^{\frac{1}{3}}$. When silica (Davison "70") was impregnated with chloroplatinic acid to give platinum contents up to 11.5% and reduced at 210°C, this relationship was observed (*12*). In the present work, when the same silica was impregnated with tetraamminepalladous nitrate and reduced at 300 or 450°C *in situ*, then the Pd area only varied as (Pd content)$^{0.4}$.

Direct evidence of crystallite sintering or aggregation is provided by electron micrographs of catalysts containing 5 or 10% Pd and reduced at 300 or 450°C (Fig. 2). Catalysts with 5% Pd show discrete palladium crystallites evenly distributed over the silica support whereas at 10% Pd loading, the crystallites form irregular agglomerates. Increasing the Pd content would not yield the expected increase in Pd area if some of the area of the larger crystallites formed at 10% Pd loading was lost by the formation of interfaces inaccessible to carbon monoxide.

Figure 1 also shows Pd areas for catalysts reduced externally at 450°C, then transferred (in air) and reduced at 450°C. This treatment would tend to sinter the catalyst more than a single *in situ* reduction, and above 5% Pd loading smaller Pd areas were observed (broken curve). As shown above, sintering or crystallite agglomeration becomes more extensive at higher metal loadings, and so the two curves in Fig. 1 diverge with increasing Pd content.

Hydrogen Chemisorption

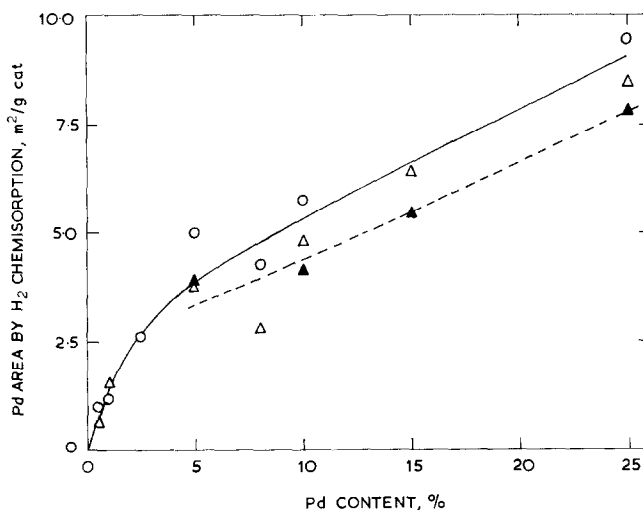Figure 3 shows the Pd area derived from hydrogen chemisorption (Table 1) as a

FIG. 3. Palladium areas from hydrogen chemisorption as a function of Pd content: catalysts reduced *in situ* at 300 (O) or 450°C (△); catalysts reduced externally at 450°C and re-reduced before hydrogen chemisorption (▲).
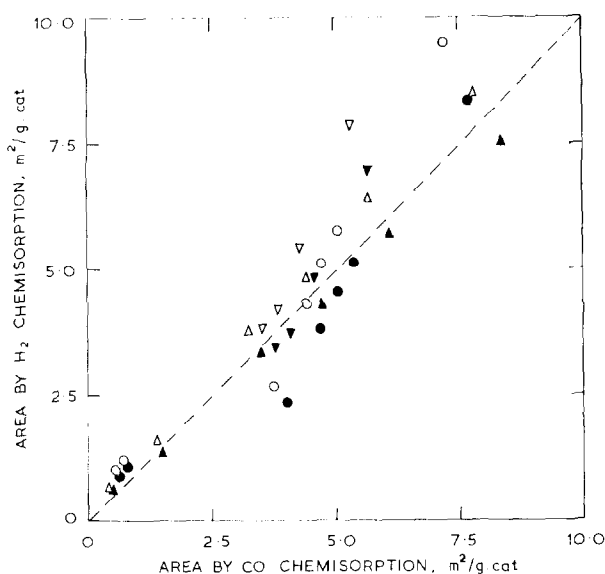
FIG. 4. Comparison of palladium areas derived from CO and hydrogen chemisorption. Open symbols assume that crystallites expose a constant mix of three low-index planes; filled symbols show the recalculation of data assuming mixture of (111) and (100) planes only. Catalysts reduced at 300 (○, ●) or 450°C (△, ▲) or externally at 450°C and re-reduced before chemisorption (▽, ▼).

function of Pd content for the same three series of catalysts, viz., catalysts reduced *in situ* at 300 or 450°C or externally at 450°C, then re-reduced. It was assumed that hydrogen was not *ab*sorbed into the palladium crystallites but only on to their surfaces with a stoichiometry of Pd_s/H = 1.0. The density of palladium surface atoms was taken as the mean value for the three low-index planes, (111), (100), and (110), viz., $1.27 \times 10^{15}/cm^2$. In this initial analysis of hydrogen chemisorption data, it is assumed (as in the case of CO chemisorption) that the "mix" of surface planes did not vary with increasing Pd content. A single curve is drawn through both sets of data for *in situ* reduced catalysts, although there is some suggestion that catalysts reduced at 450°C had slightly smaller areas than catalysts reduced at 300°C. As expected, hydrogen chemisorption areas (Fig. 3) show the same general features as CO adsorption areas (Fig. 1), including the slow growth of area with increasing Pd

content and possibly lower areas in catalysts externally reduced, transferred, and re-reduced (broken curve, Fig. 3).

A closer comparison of the magnitudes of hydrogen and CO chemisorption is made in Fig. 4. The open symbols compare Pd areas derived from CO adsorption and hydrogen adsorption using the assumptions already noted, in particular that the crystallites expose a constant mix of the three low-index planes. The filled symbols show a recalculation of the results assuming that the crystallites exposed only equal amounts of the (111) and (100) planes. Such metal crystallites might be envisaged as the cubo-octahedra with square and hexagonal faces which featured previously in the treatment of surface atom statistics (*13*). The assumption for the maximum density of adsorbed CO molecules based on data in (*9*) then becomes 0.785×10^{15} CO molecules/cm^2, and the new mean density of surface Pd atoms is $1.43 \times 10^{15}/cm^2$. The broken line in Fig. 4 shows the

ideal correspondence of Pd areas which should be found from hydrogen and CO chemisorption measurements.

There is a good correspondence between areas derived from either hydrogen or CO chemisorption with a tendency for the open symbols to lie above and the closed symbols to fall below the ideal line. It is not possible, however, to detect the need to make a *progressive* change from the assumption of a mixture of (111), (100), and (110) planes toward assuming that largely (111) and (100) planes are exposed. Therefore, it is concluded that a change in the distribution of surface planes with increasing crystallite size has not been demonstrated.

X-ray Measurements

The general correctness of the Pd areas determined by chemisorption was tested against X-ray measurements on catalysts reduced *in situ* at 450°C (Table 1). For comparison purposes, crystallite sizes were calculated from the appropriate hydrogen and CO chemisorption data assuming that the crystallites were cubes exposing five faces to the adsorbing gas. Although this assumption is arbitrary it applies a correction for loss of area due to contact with the support, and also it is not intended here to seek exact correspondence of crystallite sizes obtained by the two methods. Indeed, if there is a wide distribution of crystallite sizes then sizes from the integral breadths of X-ray line profiles are unsatisfactory when what is required is a surface-weighted mean dimension (*14*).

Figure 5 shows that crystallite sizes calculated separately from hydrogen and CO chemisorption areas and measured by X-ray line-broadening can be satisfactorily correlated. The 8% Pd catalyst which seemed to have an anomalously low hydrogen area after reduction *in situ* at 450°C (Fig. 3) now falls in place in this correlation (Fig. 5), but the X-ray size for the 15% Pd catalyst may be too high. All

points lie above the ideal (broken) line but could be moved into better correspondence by considering other crystallite shapes making less support contact (which requires a compensatory increase in the size calculated from chemisorption) or by considering an X-ray amorphous palladium fraction (which effectively decreases the mean X-ray size).

X-ray measurements also detected some interaction of palladium with the silica support when the reduction temperature was raised to 600°C. Figure 6, curve (a), shows the X-ray diffraction pattern of a 10% Pd/silica catalyst after heating at 600°C in hydrogen and cooling in flowing helium. These extra peaks were partially removed by subsequent heating to 600°C in helium [Fig. 6, curve (b)]. Only the single pure palladium peak was observed, Fig. 6, curve (c), if the high-temperature reduction (600°) was followed by oxidation (800°C in air; 3 hr), cooling in helium to 450°C, and then lower-temperature reduction (450°C; 2 hr). The diffraction pattern containing the extra peaks could not be convincingly indexed with data in the JCPDS file, but it seems possible that palladium-aided reduction of the silica is followed by the formation of a palladium-silicon intermetallic compound. There was no evidence of any palladium–silicon interaction in catalysts reduced at 300 or 450°C, on which almost all the chemisorption and catalytic measurements were carried out.

Catalyst Activity

Catalyst activities were compared in terms of the percentage of benzene hydrogenated at 100°C, taking the value from an Arrhenius plot over the appropriate temperature range, usually 75 to 150°C. Activation energies lay within a narrow range, 11 ± 2 kcal/mol, thereby minimizing uncertainty with respect to selecting an appropriate comparison temperature. Figure 7 shows the activity of a fixed weight
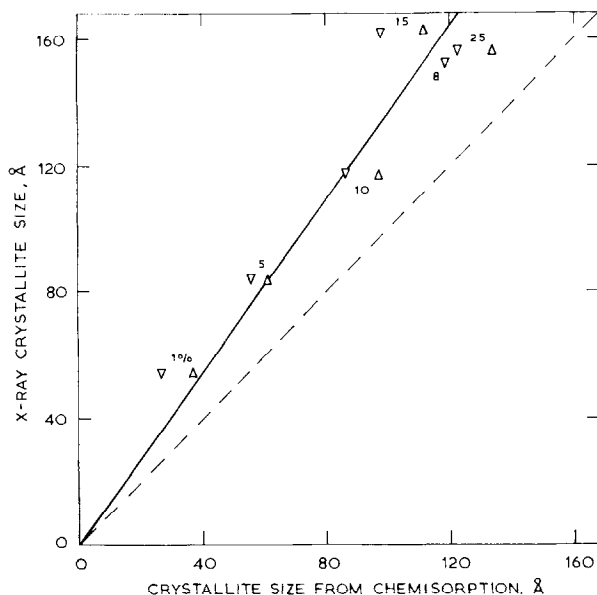
FIG. 5. Crystallite sizes from X-ray line-broadening compared with sizes calculated from CO chemisorption ($\triangle$) or hydrogen chemisorption ($\triangledown$). Pd contents of catalysts, reduced *in situ* at 450°C, indicated beside symbols.

of catalyst (0.25 g) as a function of Pd area (per fixed weight of catalyst) for two series of catalysts reduced at 300 or 450°C. Palladium areas were determined by CO chemisorption on samples actually used in the catalyst activity measurements, after discharge from the reactor, re-reducing at 300 or 450°C as appropriate. In each case there is a reasonably linear variation of activity with Pd area, i.e., near constant specific activity despite the variation of crystallite size (numbers in parentheses). For catalysts reduced at 300 or 450°C, the crystallite size ranges were 13 to 114 and 16 to 134 Å, respectively.

The effect of reduction temperature on specific activity is also shown by the two plots in Fig. 7 for catalysts reduced at 300 or 450°C. Figure 8 shows the effect on catalyst activity of extending the reduction temperature range to 550 and 250°C for catalysts prepared on Davison "70" (circles) or Porasil "A" (triangles). Clearly the specific activity is diminished by increasing the reduction temperature.

The effect could also be induced by reducing the catalyst at 300°C, testing activity, then reducing again at 450°C and retesting. A 10% Pd/silica catalyst prepared from a different palladium salt, palladous chloride, on Davison "70" silica also showed the effect, viz., specific activities of 21.0 or 7.1% benzene converted/m² Pd following reduction at 300 or 450°C. Thus the "reduction effect" was observed using different supports (Fig. 8) and different palladium salts as well as different metal loadings (Fig. 7). Other apparently relevant observations are summarized below.

It was possible to restore some of the specific activity lost on reducing at 450°C (instead of 300°C) by heating in air at 300 or 450°C followed by reduction at 300°C. However, the best increase in activity thereby achieved was only ~50% compared with the fourfold loss in specific activity. The mean values of the activation energy for the two series of catalysts reduced at 300 or 450°C appearing in Fig. 7
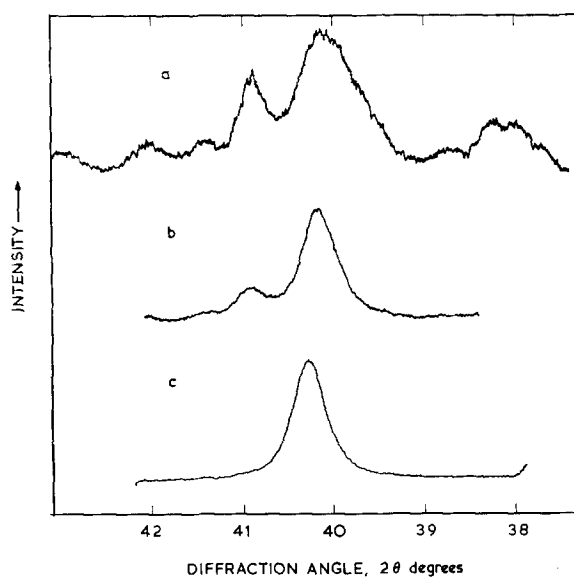
FIG. 6. X-ray diffraction profiles from 10% Pd/silica samples: (a) after reduction at 600°C; (b) after subsequent heating in helium at 600°C; (c) alternatively after subsequent oxidation at 800°C and reduction at 450°C. See text for details of procedure.
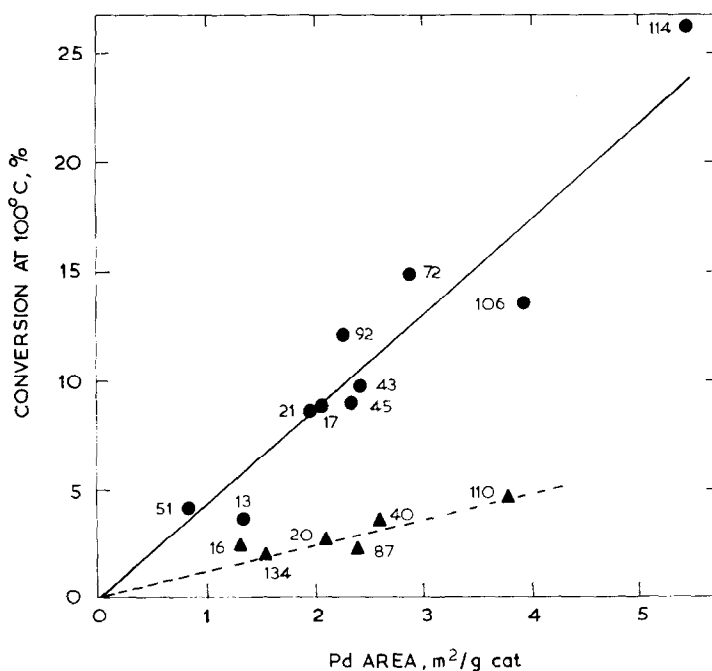

FIG. 7. Conversion of benzene at 100°C over 0.25 g samples of Pd/silica catalyst reduced at 300 (●) or 450°C (▲), as a function of Pd area (m²/g catalyst). Mean crystallite sizes calculated from CO chemisorption are shown for each catalyst.
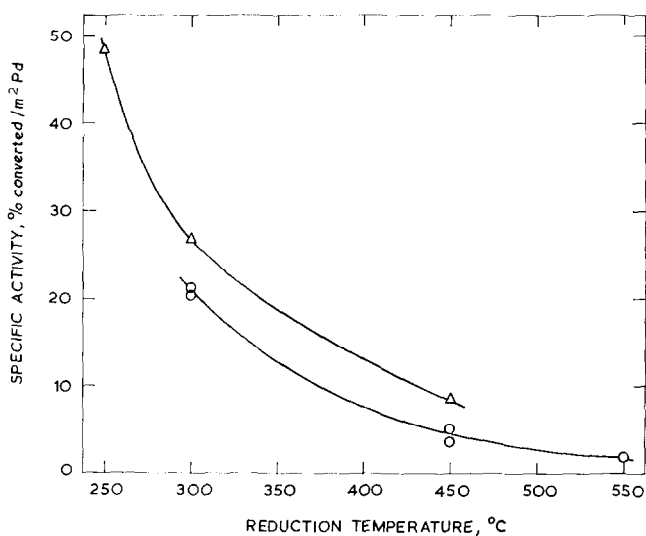
FIG. 8. Variation of specific activity for benzene hydrogenation (at 100°C) as a function of catalyst reduction temperature; 10% Pd on Porasil "A" (△) and 5% Pd on Davison "70" silica (O).

were 10.7 and 11.1 kcal/mol, respectively. Electron micrographs of catalysts reduced at 300 or 450°C (Fig. 2), for example, the two 5% Pd catalysts (a) and (b), do not reveal any evidence that reduction temperature had altered the metal distribution or dispersion. Chemisorption measurements showed quantitatively that the metal dispersion was not significantly altered, and of course it is *specific* activities which are being compared.

Specific activities were also measured for palladium/silica catalysts reduced at the same temperature (300°C) but prepared with silicas of different origins (Table 2).

All the silicas had, of course, been wetted and then dried again during catalyst preparation, but nevertheless the specific activities of the prepared catalysts show a threefold variation. There also appears to be a trend toward greater specific activity with increasing silica area.

Constant specific activity despite the variation in mean crystallite size is discussed first, starting with some comments about the possibilities for observing "crystallite size" effects. Extremely small metal crystallites may have electronic properties which differ from those of the bulk metal and so have a different specific

TABLE 2

Effect of Support on Specific Activity (10% Pd/Silica, Reduced at 300°C)

Silica	Surface area (m²/g)		Pd area (m²/g cat.)	Conversion at 100°C (%/0.25 g cat.)	Specific activity (%/m² Pd)
	Nominal	Actual			
Porasil "B"	150–200	225	3.24	6.6	8.1
Davison "70"	270–300	296	(data from Fig. 6)		17.3
Cab-O-Sil "HS5"	300–350	258	2.61	14.1	21.6
Crosfield "ID"	300–400	344	5.45	33.7	24.7
Porasil "A"	400–450	430	5.59	37.5	26.8

activity; i.e., an "electronic" crystallite size effect could occur. Baetzold (15) has reported molecular orbital calculations which suggest that palladium aggregates of up to 10 atoms have different electronic properties from bulk palladium; for example, they were expected to be better electron acceptors. The calculated values of d-band holes per atom decreased from 1.0 ($n_{Pd} = 2$) to 0.35 ($n_{Pd} = 8$). This type of crystallite size effect would not be expected in the present work involving larger crystallites, but an effect could arise from variation in surface structure, as suggested by models of perfect crystallites in the size range below $\sim$40 Å and to a lesser extent up to 70 Å. Unfortunately imperfect crystallites formed from random numbers of palladium atoms may largely obscure the observation of this second type of crystallite size effect. Hence, some experimental evidence for the variation of surface structure with crystallite size seems essential, but as discussed previously no evidence of this was found. Therefore, it could be argued that it is not unexpected that the specific activity is independent of crystallite size for each series of catalysts with a common reduction temperature, 300 or 450°C.

It has been shown previously by Aben et al. (2) that the specific activity of palladium supported on silica or alumina at dispersions in the range of $H/Pd_{(total)}$ from $\sim$0.8 to <0.1 was also constant at 100°C for benzene hydrogenation under rather different conditions (5.6 atm H_2, 0.4 atm benzene). It is interesting to note that the dispersion had been varied by subjecting samples of the catalyst (previously calcined at 500°C in air) to subsequent thermal treatment in hydrogen at 500–800°C (and re-reduction at 100°C before testing). In the present work, constant specific activity depended on the use of a fixed reduction temperature, but no calcination stage was employed. From the kinetic data given in (2), the turnover number on palladium at 100°C and 1 atm of hydrogen is 5.7×10^{-3} benzene molecules/surface Pd atom/sec. In the present work the turnover numbers under the same conditions are 14.1×10^{-3} and 3.8×10^{-3} for the two series of catalysts (Fig. 7) reduced at 300 and 450°C. This is satisfactory agreement particularly as the turnover number from data in (2) lies nearer the present value for catalysts reduced at 450°C.

The effect of reduction temperature on specific activity is considered next in terms of the following possible explanations: (i) variation in the surface structure of the support, (ii) the effect of activators or inhibitors which arise from the palladium precursor or the support, and (iii) interaction between palladium crystallites and the support.

(i) It may be that the "reduction effect" observed in the present work is in reality some sort of "support effect." Benzene adsorption on silica is sensitive to the dehydroxylation of the surface and was much less on silica samples heated above 500°C compared with samples heated at 200 to 500°C (16). A support effect was observed recently (17) for benzene hydrogenation over Pd/Al_2O_3 and Pd/SiO_2 catalysts, the former being about twice as active, but impurities in the silica (see below) may have been responsible. The absence of a support effect for the same reaction over other Pd/Al_2O_3 and Pd/SiO_2 catalysts reported earlier (2) may be connected with the initial calcination of catalysts at 500°C during preparation, followed by high-temperature reduction at 500 to 800°C.

(ii) A similar effect of reduction temperature on specific activity was observed for ethylene hydrogenation over platinum/silica catalysts (18). Further it has recently been reported that platinum on silica reduced above 300°C retains hydrogen chemisorption capacity but loses ability to

catalyze ethylene hydrogenation, due perhaps to dispersion into clusters below the critical size for ethylene chemisorption (*19*). The catalysts used in the work described in Ref. (*18*) had been prepared from chloroplatinic acid, and residual chlorine appeared to be involved in the effect. However, for benzene hydrogenation over platinum/alumina catalysts, Basset *et al.* (*3*) found no effect of chlorine content in the range 0 to 0.5×10^{-3} g Cl^-/g catalyst. In the present work most catalysts were prepared with tetraamminepalladous nitrate, but catalysts prepared from palladous chloride had approximately the same specific activity, i.e., 21.0% converted/m^2 Pd after reduction at 300°C, compared with a value of 17.3% for catalysts prepared from the nitrate (Fig. 7).

It was also found recently that traces of iron and sulfate (normally present in Davison "70") when added to purified alumina modified the catalytic properties of palladium (*17*), *to an extent dependent upon the reduction temperature.* This could be a significant observation for the present work including results with catalysts prepared on different silicas (Table 2), but it has also to be noted that reduction of palladium on Davison "70" silica itself at temperatures between 300 and 650°C did not alter significantly the benzene hydrogenation activity (*17*).

(iii) X-ray diffraction suggested apparent interaction of palladium with the silica support once the reduction temperature has been taken to 600°C (Fig. 6). It is then necessary to assume that some interaction of palladium and silicon occurred at temperatures below 600°C (and more so at 450°C compared with 300°C) in order to explain the "reduction effect." As chemisorption capacity was not affected significantly by reduction at 450°C compared with 300°C (Figs. 1 and 3) the effect of silicon insertion into palladium might be envisaged as the disruption of the palladium ensembles required for benzene adsorption.

If a single palladium atom is the active site, then its properties might be modified by the presence of silicon atoms. The partial restoration of activity lost after 450°C reduction by oxidation and reduction at 300°C might be explained in terms of silicon removal on re-oxidation. It must be emphasized, however, that there was no evidence from X-ray diffraction of any palladium–silicon interaction in catalysts reduced at 300 or 450°C.

Clearly further work is needed to determine why the temperature at which supported metal catalysts are reduced appears to depress the activity per unit area of exposed metal surface in some catalytic hydrogenation reactions.

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