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Palladium Areas in Supported Catalysts

Determination of Palladium Surface Areas in Supported Catalysts by Means of Hydrogen Chemisorption

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Hydrogen chemisorption is a suitable tool for the determination of palladium surface areas in supported catalysts provided that chemisorption conditions are carefully chosen. The method can also be used to determine surface areas of particles of a size where other techniques, such as electron microscopy, X-ray line-broadening and small-angle scattering, often fail through interference of the support.

Combined surface area and hydrogen chemisorption measurements made on palladium-black samples show that under the conditions applied about one hydrogen atom is adsorbed on each palladium atom exposed. This finding is confirmed by electron microscopy.

INTRODUCTION

For a thorough understanding of the behavior of supported metal catalysts we need to know the degree of dispersion of the metal. This parameter can be expressed as the specific metal surface area or the average metal crystallite size. Hydrogen chemisorption has proved a useful tool for the determination of the surface area of supported platinum (*1–3*) and nickel (*4–6*). But it has hitherto not been possible to apply this technique to supported palladium, because the hydrogen tends to be absorbed (*7*).

Scholten *et al.* (*7*) have proposed the use of carbon monoxide as an adsorbate. These investigators found reasonable agreement between Pd crystallite sizes on various carriers as derived from CO chemisorption and determined by electron microscopy and X-ray line-broadening. In our opinion, however, this method has several drawbacks, of which we mention two:

(1) CO can be chemisorbed on alumina (which is a common support) to such an extent as to require a considerable correction for the blank, in particular for samples with a low Pd content. This correcting procedure may have an adverse effect on the accuracy of the chemisorption results.

(2) The ratio of adsorbed CO to exposed palladium is not constant and varies with the support (*8*) and it may even be that it also varies with the dispersion, as has been observed for Pt (*21*).

The present study was made to try and modify the hydrogen chemisorption technique so as to exclude the disturbing effect of absorption of hydrogen by the metal. Prior to a discussion of our experimental results a few introductory remarks on the palladium-hydrogen system seem appropriate.

THE PALLADIUM-HYDROGEN SYSTEM

In Fig. 1 we present a series of isotherms of the system hydrogen-palladium (*10, 11, 26*). The steep branches of each isotherm represent two solid solutions (α- and β-palladium hydride phases) separated by a region of coexistence of these two phases. The constitution of the various phases has been established by X-ray diffraction (*12*).

From the absorption isotherms given in Fig. 1 it is clear that if we want to exclude interference of absorption during chemisorption measurements we have to carry out the experiments at elevated temperatures and low hydrogen pressures, for example, at 70°C and a hydrogen pressure of 1 mm Hg. Under these conditions the maximum amount of hydrogen that can be absorbed amounts to about 0.002 atom of hydrogen per palladium atom (*25*).

EXPERIMENTAL

Chemisorption Technique

The measurements were carried out in a conventional static-sorption apparatus as described in ref. (*4*).

Reduction. Samples were reduced with hydrogen at 400°C under atmospheric pressure for 1 hr.

Evacuation. Samples were evacuated (to 10^{-6} Torr) for 16 hr at 400°C. An evacuation temperature of 400°C was adopted on the basis of the following observations: 2 wt% palladium/silica samples were prereduced at 580°C for 3 hr and subsequently evacuated at a given temperature; then we determined the amount of hydrogen that could be adsorbed at 70°C and 1 mm Hg; finally we desorbed at 650°C. Desorption at 650°C always released the same amount of hydrogen for the given palladium/silica sample. Desorption at 580°C gave the same value, which shows that after evacuation at 580°C the palladium surface must be clean. The lower adsorption capacity after evacuation at 400°C and 300°C—3% and 11%, respectively—must therefore be ascribed to incomplete removal of H_2 at these temperatures. Since at 400°C the error introduced by this phenomenon falls well within the limits of overall accuracy of the determination, we chose 400°C as the maximum pretreatment temperature in order to reduce the danger of sintering to a minimum.

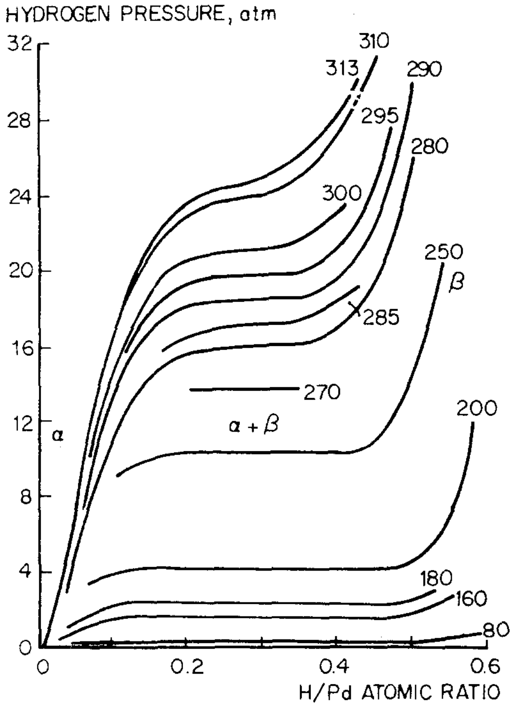

FIG. 1. Hydrogen-palladium isotherms from 80° to 313°C. [Data of Gillespie, Sieverts, and others quoted by Gibb (10).]

Hydrogen adsorption. After the evacuation the sample was cooled to 70°C and hydrogen introduced from a calibrated vessel in such a way that a constant hydrogen pressure of 1 mm Hg was maintained. The amount of hydrogen adsorbed was found as the difference of two determinations, viz. one on the sample and one under equal conditions on the bare carrier (the blank). For the carriers used no adsorption of hydrogen was observed at 70°C.

Catalyst Preparation

Impregnation. $PdCl_2$ was dissolved in concentrated HCl, the excess HCl evaporated, and the palladium compound (H_2PdCl_4) redissolved in water. The supports were impregnated with the resultant solution by means of a dry impregnation technique. Subsequently the catalyst was dried at 120°C for 3 hr and calcined at 500°C for a further 3 hr.

The palladium-black was made via the Willstätter method (*27*).

Ion exchange. A solution of 0.001 *M* Pd $(NH_3)_4Cl_2$ was stirred with 50 g of support for 10 min in a nitrogen atmosphere. Over a period of 1½ hr 937 ml of a solution 0.01 *M* in $Pd(NH_3)_4(OH)_2$ and 0.001 *M* in $Pd(NH_3)_4Cl_2$ was added. The resulting mixture was stirred for 1 hr. The solids were filtered and washed four times with 150 ml water.

The catalyst was dried at 120°C for 3 hr and calcined at 500°C for the same period.

TABLE 1
Survey of Catalysts Used in Present Investigation

Support	Pd (wt%)	Catalyst preparation	H/Pd
Al_2O_3	15	Impregnation	0.28
Al_2O_3	5	Impregnation	0.41
Al_2O_3	2	Impregnation	0.41
Davison silica (grade 70)	5	Impregnation	0.24
Davison silica (grade 70)	2	Impregnation	0.40
Davison silica (grade 70)	2.2	Ion exchange	0.63
Davison silica (grade 70)	0.53	Ion exchange	0.83

Table 1 presents a survey of catalysts included in this investigation.

The alumina- and silica-supported palladium catalysts of relatively low hydrogen /palladium ratio have been prepared from the more highly dispersed samples by a sintering technique in hydrogen. Details are given in Table 2.

TABLE 2
Influence of Temperature on Sintering of Palladium in a Hydrogen Atmosphere

Sintering temperature,[a] T (°C)	H/Pd	
	5 wt% Pd/Al_2O_3	2 wt% Pd/SiO_2
400	0.41	0.40
600	0.15	0.30
800	0.06	0.13
900	—	0.08

[a] Temperature at which catalysts were heated in atmospheric hydrogen for 20 hr.

Results and Discussion

A. *Hydrogen-Palladium Isotherms for Supported and Unsupported Palladium*

To find out whether the absorption behavior of palladium on a support is similar to that of palladium-black, we have compared the hydrogen isotherms for two palladium-on-silica catalysts and a palladium-black catalyst (surface area less than 0.1 m^2/g), both determined at 70°C. Results are presented in Fig. 2. The similarity in slope of the branches indicated by I strongly suggests that in both cases the same phenomenon is involved. For the palladium black this is known to be the absorption of hydrogen by the palladium lattice to form α-Pd-H. The difference in shape of the branches III of the absorption isotherm of supported and nonsupported palladium probably stems from a spread in crystallite size of the former. Branch II is the adsorption part of the isotherm.

From the results given in Fig. 2 it is interesting to note that at 70°C the hydrogen content of the β phase decreases when going from coarse (≫500 Å) to finely divided Pd (~130 Å and 25 Å, respectively). The sorption experiments at −78°C for finely divided Pd (~25 Å) on

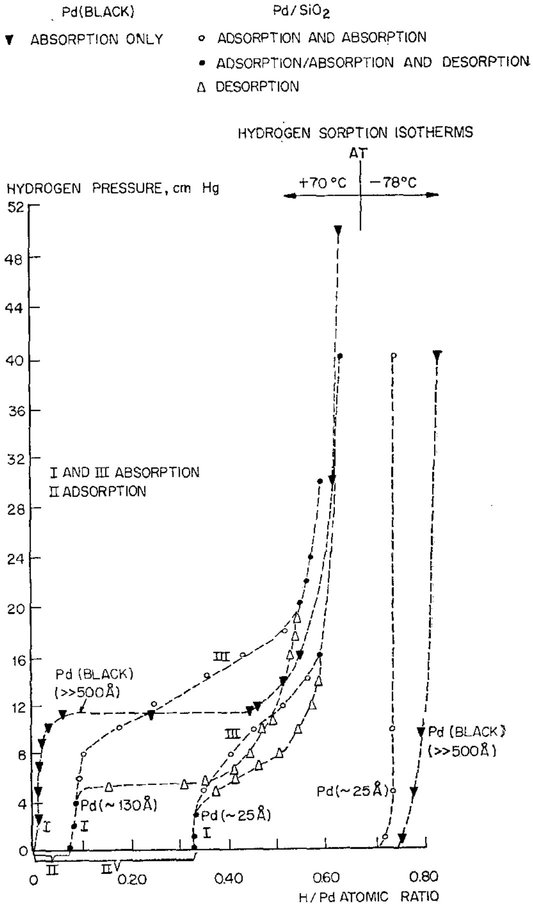

Fig. 2. Hydrogen-palladium isotherms for supported and unsupported palladium.

SiO_2 and Pd black ($\gg$500 Å) confirm that the smaller particles absorb less hydrogen in the β phase than the larger ones. The total hydrogen uptake by the smaller particles is smaller even with a much higher contribution of the adsorption. This phenomenon would be an interesting subject for further study. In addition, at $-196°C$ extremely high hydrogen sorption values were obtained for finely divided Pd ($\sim$25 Å) on SiO_2 ranging from H/Pd values of 1 to 4 at 2 and 40 cm Hg hydrogen pressure, respectively . These high values are due to the hydrogen uptake of the SiO_2 carrier at $-196°C$. After correction for the blank the H/Pd values at $-196°C$ are very close to the values obtained at $-78°C$. The high sorption values (H/Pd $\sim$ 2) mentioned by Turkevich (*28*) and Scholten (*9*) may be due to this phenomenon.

Suzuki and Yasumori (*13*) give a method for determining the palladium surface area in palladium catalysts by the use of the hydrogen isotherm. They describe the first branch of the isotherm, where only the α-phase exists, by the following equation:

$$\text{amount sorbed} = k_1P \text{ (adsorption)} + k_2\sqrt{P} \text{ (absorption)}$$

where P is the hydrogen pressure and k_1 and k_2 are constants for a certain catalyst. These calculations are based on two assumptions: adsorption is proportional to the hydrogen pressure, and α–β phase transition takes place at a constant pressure.

The first assumption does not seem realistic in view of the fact that in similar systems (*14*) chemisorption levels out at pressures which are much lower than those applied by the Japanese workers. The second assumption is clearly at variance with the experimental facts for supported palladium (Fig. 2). Hence, we reject the recommended method, which involves measurements at various pressures.

B. *Correlation between Chemisorption Data and Hydrogenation Activities*

If the measured H/Pd ratio is a good yardstick of exposed palladium metal one expects it to correlate with the hydrogenation or dehydrogenation activity in the same way as found for supported metals (*15–20*). For a number of supported palladium samples both the H/Pd ratio and the activity for benzene hydrogenation were determined. In all cases we determined the hydrogenation activity of those samples which had previously been subjected to the hydrogen chemisorption measurements.

We found a linear relationship between hydrogenation activity and the fraction of Pd atoms that are exposed. These results will be published together with data obtained over Pt and Ni catalysts (*22*).

C. *Determination of the Number of Hydrogen Atoms Adsorbed per Atom of Exposed Palladium*

The overall H/Pd value, i.e., the ratio of the number of hydrogen atoms adsorbed to the total number of palladium atoms, can be converted into the ratio of atoms exposed to the total number of atoms present (a value which determines the specific metal surface area), if the number of hydrogen atoms adsorbed per *exposed* palladium atom is known. We have determined this parameter by measuring the amount of hydrogen chemisorbed on a palladium-black sample of known surface area (BET, N_2). The results given in Table 3 show that the ratio of hydrogen atoms adsorbed to palladium atoms exposed is practically 1. There is some uncertainty in this ratio because of the following reasons:

(a) The number of Pd atoms per cm^2 varies between 0.94×10^{15} and 1.54×10^{15} for the (110) and the (111) plane, respectively; as an average we have taken 1.2×10^{15} Pd atoms per cm^2, which may introduce an uncertainty of maximum 15% in the H adsorbed per Pd exposed ratio.

(b) The area chosen for the nitrogen molecule gives rise to an additional uncertainty of about 10% in the H/Pd ratio.

D. *Comparison of Palladium Particle Sizes Derived from Hydrogen Chemisorption and Electron Microscope Data*

We have calculated the average particle size of palladium crystallites on a support from hydrogen chemisorption data on the basis of a one-to-one ratio of hydrogen atoms adsorbed to palladium atoms

TABLE 3

CALCULATION OF RATIO OF HYDROGEN ATOMS ADSORBED TO PALLADIUM ATOMS EXPOSED FROM BET (N_2) SURFACE AREA AND HYDROCHEMISORPTION MEASUREMENTS ON TWO PALLADIUM-BLACK SAMPLES[a]

Surface area of palladium black, (m^2/g) (BET method N_2 molecule: 16.27 A^2)	Calculated ratio[b] of palladium atoms exposed to total number of palladium atoms	Hydrogen sorption,[c] ratio of hydrogen atoms sorbed to total number of palladium atoms			Ratio of hydrogen atoms adsorbed to palladium atoms exposed
		Adsorbed + absorbed	Absorbed[d]	Adsorbed	
5.8	0.0123	0.0145	0.0020	0.0125	1.02
15.4	0.033	0.037	0.0020	0.035	1.05

[a] Prior to the hydrogen sorption and BET surface area measurement the palladium-black was reduced with hydrogen (1 atm) and subsequently evacuated at 130°C (10^{-6} mm Hg).

[b] Calculated on the basis of 1.2×10^{19} palladium atoms per square meter (*23*, *24*). This is the mean value for the crystallographic planes (100), (110), and (111).

[c] Sorption conditions: temperature, 70°C; hydrogen pressure, 1 mm Hg. The amount of hydrogen sorbed at 70°C is determined by desorption at 600°C. It is impossible to measure sorption direct, since at the highest temperature that can be applied during evacuation of the sample without sintering (130°C) some hydrogen remains adsorbed on the surface.

[d] Interpolated from G. H. Nernst's results (*25*).

TABLE 4

COMPARISON OF PARTICLE SIZES IN SUPPORTED PALLADIUM DETERMINED BY MEANS OF HYDROGEN CHEMISORPTION AND ELECTRON MICROSCOPY[a]

Catalyst composition	Pretreatment temperature, (°C)	Experimental H/Pd value[b]	Particle size, (Å) (calculated[c] from H/Pd ratio)	Particle size, (Å) (Electron microscopy[d])
2%w Pd/SiO_2	400	0.40	22	<25
2%w Pd/SiO_2	800	0.13	68.5	65
5%w Pd/Al_2O_3	400	0.41	22	<25
5%w Pd/Al_2O_3	800	0.06	148	130

[a] Prior to chemisorption the samples were evacuated at 400°C for 16 hr (10^{-6} mm Hg).

[b] Sorption conditions: temperature, 70°C; hydrogen pressure, 1 mm Hg.

[c] Calculation based on the following assumptions: atomic ratio of hydrogen adsorbed to palladium exposed = 1; 1 m^2 of palladium comprises 1.2×10^{19} atoms; cubic palladium particles having five exposed faces; particle density of palladium on supported catalyst is that of bulk palladium (12.0 g/cm^3). These assumptions resulted in the formula: $\bar{d} = 10 \times 0.885/\mathrm{H/Pd}$ Å ($\bar{d}$ is the average cubic edge).

[d] Samples contain palladium particles of a very narrow Gaussian distribution.

exposed. Details of the calculation method are given in Table 4. Calculated particle sizes are compared with experimental values obtained by electron microscopy. Since the latter method does not allow of determining particles smaller than some 25 Å through interference of the support, we have sintered the finely dispersed palladium present in the original samples (see Table 4) by heating in a hydrogen atmosphere.

The linear relationship between H/Pd values and hydrogenation activities and the excellent correlation between particle sizes derived from chemisorption data and electron microscopic measurements warrant the conclusion that the chemisorption method described in this paper yields reliable values for palladium particle sizes or surface areas.

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