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Hydrogen–Oxygen Titration Method for the Measurement of Supported Palladium Surface Areas

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The titration by means of hydrogen or deuterium at 100°C of oxygen preadsorbed on a supported palladium catalyst has been used to measure the dispersion of the palladium. Results agree with those obtained by X-ray line broadening and chemisorption of oxygen or carbon monoxide. The titration, which is done at pressures where a negligible amount of bulk hydride forms, has distinct advantages over the other methods.

INTRODUCTION

For many of the Group VIII metals techniques have been developed to measure the metal surface area in supported catalysts. These measurements are important since from them one may assess the dispersion D defined as the fraction of the total number of metal atoms which are at the surface of the metal particles. In turn, the rate of a reaction performed on a catalyst may, with some reasonable assumptions, be expressed as a turnover number (*1*).

One technique that has been used to measure metal surface area is the selective chemisorption of hydrogen or carbon monoxide. The work of Sinfelt (*2*) is a notable example in which such measurements on 11 different supported metals allowed these metals to be arranged in relative order of catalytic activity for ethane hydrogenolysis. Another method, the titration of adsorbed oxygen by hydrogen, was originally developed for supported platinum (*3*) and has recently been extended to supported rhodium (*4*). In both of these methods a standard volumetric adsorption apparatus also used routinely for BET measurements is usually employed, and the measurements are normally done at or near room temperature and in a pressure range from 7 to 100 kPa. (The symbol kPa stands for kilopascal or $10^3 \times$ Newton m^{-2} and 1.000 kPa = 7.500 Torr.)

Of the common catalytic metals palladium is unique in its ability to dissolve hydrogen to form one of two hydrides, the β-phase hydride, at room temperature and hydrogen pressure above about 2 kPa (*5*). To avoid the formation of this hydride at 303 K the pressure must be kept below 2.27 kPa, under which conditions hydrogen dissolves only sparingly to form the α-phase hydride (*6*). Clearly, hydrogen chemisorption and the hydrogen titration as described above cannot be employed for palladium unless corrections are made for the hydrogen taken up to form the β-phase hydride. Sinfelt and Yates have correlated hydrogen and carbon monoxide adsorption for some of the catalysts they studied, but this was not done for palladium (*7*). If one assumes that the hydrogen titration occurs for palladium as it does for platinum (*3*) and if one ignores the solubility to calculate an apparent dispersion D_a, it is easy to show that the true dispersion D is related to the apparent dispersion by the relation $D = D_a - m/3$, where m is the solubility, equal to the ratio of the number of hydrogen atoms taken up into the bulk to the total number of palladium atoms. Although the solubility of hydrogen in palladium has been extensively studied for bulk palladium (*8*), the corrections are prohibitively large for poorly dispersed catalysts in which the ratio of bulk to surface palladium is large. Furthermore, Aben has reported that the solubility appears to depend on the particle size of palladium for palladium/silica catalysts and palladium black (*9*), and as a consequence the correction becomes uncertain, particularly for well-dispersed catalysts although the correction becomes smaller as D goes up. Carbon monoxide adsorption has the drawback that carbon monoxide may adsorb in linear and bridged forms. Indeed, Eischens, Francis and Pliskin (*10*) have reported the existence of both forms on palladium as determined by ir studies, and Clarke, Farren and Rubalcava have reported that the relative amount of the bridged form changes with palladium particle size in a series of silica-supported catalysts (*11*).

To circumvent these difficulties the conditions under which the surface area measurements are normally carried out have been modified to avoid the formation of the β-phase hydride. For example, Aben (*9*) has measured the surface areas of palladium black and palladium supported on silica and alumina by hydrogen chemisorption at 343 K and 0.133 kPa, and Sermon (*12*, *13*) has used a combination of hydrogen titration and hydrogen chemisorption at 273 K and 303 K at pressures up to 0.533 kPa for surface area measurements on palladium blacks of widely different surface areas. Under such conditions the very small amount of hydrogen in the α-phase may then be ignored or corrected for. Unfortunately, the usual volumetric adsorption apparatus cannot be used because of the low pressures needed to prevent the formation of the β-phase hydride.

The pressure above which the β-phase begins to form is a strong function of temperature, and in addition palladium exhibits a large isotope effect in its behavior towards deuterium. As already mentioned, at 303 K the β-phase starts to form at 2.27 kPa of hydrogen whereas 10.67 kPa of deuterium are required (*14*); at 373 K the β-phase does not begin to form until the hydrogen pressure reaches 46.7 kPa and the deuterium pressure reaches 144 kPa (*15*). Thus, *it should be possible to use the hydrogen titration at pressures below 46.7 kPa or a deuterium titration below 144 kPa without any modification in the usual adsorption apparatus so long as the catalyst sample is maintained at the easily controlled temperature of 373 K.*

By employing this modification of raising the temperature to 373 K we have measured the dispersion of a commercial palladium/alumina catalyst by titration with both hydrogen and deuterium. These results are compared with dispersions measured on the same catalyst by the chemisorption of oxygen and carbon monoxide at room temperature and by X-ray line broadening. Two other estimations of the dispersion of the catalyst were also made. Both rely on our observation that the β-phase hydride could be destroyed by pumping for a short time at room temperature whereas surface hydrogen was not removed to any appreciable extent. It was thus possible to estimate the amount of hydrogen on the surface by measuring the total sorption, composed of adsorption and absorption, and subtracting from it the amount of hydrogen absorbed back into the catalyst after pumping. It was also possible to perform a "reverse" titration of adsorbed hydrogen with oxygen at room temperature by destroying the β-phase by pumping and titrating the hydrogen left on the surface with oxygen.

EXPERIMENTAL METHODS

The experiments were carried out in a conventional volumetric adsorption apparatus which has already been described (*3*). The source, purity and purification of the gases used, including helium used for dead space determinations, are given in Table 1. The catalyst was a commercial one obtained from Engelhard Industries and contained nominally 5% palladium by

TABLE 1

PURIFICATION OF GASES

Gas	Source	Purity %	Further purification
H_2	Liquid carbonic	99.93	Pd-diffused
D_2	Matheson (CP)	99.5	Pd-diffused
O_2	Matheson (Research Grade)	99.999	None
CO	Matheson (CP)	99.5	Passed through Dry Ice–acetone bath
He	Liquid carbonic (Grade A)	99.995	Passed over hot Cu wire and through a liquid nitrogen trap

weight supported on alumina (lot No. 19638). Two series of experiments were performed on two separate batches of about 0.6 g of the catalyst as received, designated as I and IIa. Sample IIa was used for three more series of experiments designated as IIb through IId.

Table 2 gives the experiments done on each sample in the order in which they were performed and the conditions of reduction and outgas used before each experiment. For the heating schedule a linear heating rate of 0.025 K s^{-1} was used throughout. In the initial reduction of I and IIa the samples were first outgassed for 0.5 hr at room temperature, approximately 298 K; the temperature was then increased to 653 K. The catalysts were treated in about 21 kPa of static oxygen for 5 min when the temperature reached 573 K and then evacuated as the temperature rose from 573 to 653 K. The samples were reduced in flowing hydrogen (1.0 cm^3 s^{-1}) and outgassed under the conditions given in Table 2. The other reductions were carried out in about 47 kPa of static hydrogen or deuterium (for samples IIc and IId). After outgassing, the samples were cooled *in vacuo* to the temperature of the sorption experiment. Samples IIb and IIc had been exposed to air at room temperature for about 3 wk after use. It should be noted that in Expts 7, 8, 12, 13 and 15 it was not necessary to reduce and outgas the palladium surface; either a hydrogen- or deuterium-covered surface was desired at the start of these experiments, or hydrogen or deuterium left on the surface was re-

TABLE 2

PRETREATMENT CONDITIONS

Sample	Expt	Technique to be employed	Reduction		Outgas	
			Time (hr)	Temp (K)	Time (hr)	Temp (K)
I	1	O_2 adsorption	2	653	18	653
	2	CO adsorption	2	Room	16	653
IIa	3	O_2 adsorption	2	653	14.5	653
	4	O_2 adsorption	12	Room	2	653
	5	CO adsorption	2	Room	2	653
IIb	6	H_2 sorption	0.33	623	3	653
	7	H_2 back-sorption	—	—	0.5	Room
	8	O_2 titration	—	—	0.5	Room
	9	CO adsorption	12	Room	2	653
IIc	10	D_2 titration	12	Room[a]	2	653
	11	D_2 sorption	—	—	2	653
	12	D_2 back-sorption	—	—	0.33	Room
IId	13	D_2 titration	1	373	0.5	373
	14	O_2 adsorption	—	—	2	653
	15	H_2 titration	—	—	—	—

[a] Reduced in static deuterium.

acted off by oxygen before performing a titration.

Hydrogen and deuterium titrations at 373 K were performed by the method of Benson and Boudart (*3*); after the pretreatments in Table 2, the samples were exposed to approximately 47 kPa of oxygen at either room temperature (Expt 10) or 373 K (Expts 13 and 15) for 1 hr. The catalyst chamber was then evacuated at the same temperature for 1 hr before the titrations were performed. The temperature was controlled at 373 K by means of a large beaker of boiling water, and care was taken to maintain the same water level by adding small amounts of hot water. The sample was kept in the water bath for 1 hr before titrating to be sure its temperature was 373 K. It was necessary to add the titrants slowly and to avoid sudden pressure increases to be sure the sample was not cooled down enough to start the formation of the β-phase. Carbon monoxide and oxygen adsorptions were done at room temperature, and all the isotherms were measured 1 hr after exposure to the gas being used. For the isotherms taken at 373 K an apparent dead volume at 373 K was measured (*16*).

One qualitative experiment was done to see if the β-phase could be destroyed rapidly by pumping at room temperature. At the conclusion of Expt 5 the temperature of the catalyst was programmed up to 653 K while pumping and then maintained at 653 K for 18 hr. After cooling to room temperature, hydrogen was admitted at about 47 kPa, under which conditions the β-phase forms. The catalyst was then pumped on for 12 min until the pressure was about 0.01 kPa above the sample. Provided the destruction of the β-phase was fast, only a small amount of hydrogen should have been left in the palladium. The sample was isolated from the pumps and the temperature was programmed up to 653 K and held at that temperature for 21 hr to destroy any remaining β-phase. As discussed below, it was concluded that a negligible amount of hydride appeared to be left after this short period of pumping at room temperature but that hydrogen on the palladium surface was not significantly removed.

The results of the experiment described above permitted us to determine the amount of hydrogen back sorbed into the catalyst. The total sorption (both absorption and adsorption) was first determined at room temperature. The catalyst was pumped on at room temperature for 20–30 min to destroy the β-phase, after which the absorption isotherm was determined. The difference in the two isotherms thus was a measure of the amount of surface hydrogen. Following the determination of the amount of surface hydrogen by the back-sorption experiment, the β-phase was again destroyed by another short evacuation at room temperature, and a reverse titration of the hydrogen remaining on the palladium surface with oxygen was performed at room temperature in a manner similar to the hydrogen and deuterium titrations.

X-Ray line broadening measurements were obtained on portions of samples I and IIc after Expts 2 and 12. The profile of the palladium (220) reflection was obtained with a Picer X-ray diffractometer. Nickel-filtered copper radiation was collimated through 4° Soller slits, 1° beam slits and a 0.2° receiving slit; the scanning speed was 0.0083° s^{-1} (2θ). The breadth at half-maximum intensity was corrected for instrumental broadening (using the 112 α-quartz reflection) by Warren's method, and the particle size was calculated from the Scherrer equation by using a shape factor of 0.9 (*17*).

RESULTS

Typical isotherms for the various sorption techniques are shown in Figs. 1 and 2. For oxygen adsorption, oxygen titration, carbon monoxide adsorption, hydrogen titration and deuterium titration, the net uptakes were obtained by extrapolating the isotherms to zero pressure to correct for physical adsorption on the support.

The qualitative experiment described in the previous section in which the β-phase hydride was destroyed by pumping gave a very interesting result. After pump-

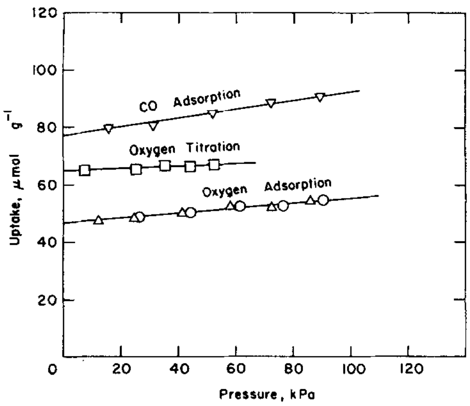

FIG. 1. Oxygen adsorption, oxygen titration and carbon monoxide adsorption at room temperature: (○) Expt 3 (after outgassing for 14.5 hr at 653 K); (△) Expt 4 (after outgassing for 2 hr at 653 K); (□) Expt 8; (▽) Expt 9.

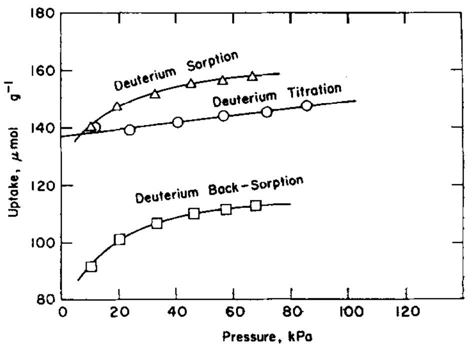

FIG. 2. Deuterium sorption, deuterium back sorption and deuterium titration: (○) Expt 10; (△) Expt 11; (□) Expt 12.

ing at room temperature for 12 min and heating to 653 K, the catalyst evolved approximately 12 μmol H_2 g^{-1}. Since the sample had originally taken up over 150 μmol H_2 g^{-1} it is obvious that the very large amount of hydrogen which dissolved to form the β-phase had most likely been completely removed. Thus, it was possible to measure the amount of surface palladium by the back-sorption technique. For hydrogen and deuterium sorptions and back-sorptions, the uptakes on the palladium surface were obtained from the difference in uptakes at 53.3 kPa because of the curvature of the isotherms.

The experimental results are given in Table 3 as micromoles of H_2, D_2, O_2 and CO taken up per gram of dry catalyst. X-Ray line broadening gave average particle diameters of 6.0 and 6.1 nm for the samples taken after Expts 2 and 12, respectively.

DISCUSSION

In order to translate the uptakes in Table 3 into dispersions we have assumed

TABLE 3

SUMMARY OF EXPERIMENTAL RESULTS

Expt	Technique employed	Uptake temp (K)	Uptake (μmol g^{-1})	Dispersion
1	O_2 adsorption	Room	47	0.20
2	CO adsorption	Room	83	0.18
	X-Ray			0.15
3	O_2 adsorption	Room	47	0.20
4	O_2 adsorption	Room	47	0.20
5	CO adsorption	Room	84	0.18
6	H_2 sorption	Room	167	0.19
7	H_2 back sorption	Room	123	
8	O_2 titration	Room	65	0.18
9	CO adsorption	Room	76	0.16
10	D_2 titration	373	136	0.19
11	D_2 sorption	Room	157	0.19
12	D_2 back sorption	Room	111	
	X-Ray			0.15
13	D_2 titration	373	149	0.21
14	O_2 adsorption	373	46	0.20
15	H_2 titration	373	151	0.21

throughout a set of stoichiometries for the various kinds of sorption experiments as follows where subscript s denotes a surface palladium atom and H denotes either hydrogen or deuterium:

Oxygen adsorption: $$Pd_s + \tfrac{1}{2}O_2 \rightarrow Pd_sO, \qquad (1)$$

CO adsorption: $$Pd_s + CO \rightarrow Pd_sCO, \qquad (2)$$

Hydrogen or deuterium titration:
$$Pd_s + \tfrac{3}{2}H_2 \rightarrow Pd_sH + H_2O, \qquad (3)$$

Oxygen titration:
$$Pd_sH + \tfrac{3}{4}O_2 \rightarrow Pd_sO + \tfrac{1}{2}H_2O. \qquad (4)$$

It has been further assumed that pumping at room temperature after a hydrogen or deuterium sorption removed all but a negligible amount of hydrogen or deuterium dissolved in the palladium without removing any significant amount of hydrogen or deuterium held on the surface of the palladium. Consequently, the difference between the sorption and back-sorption uptakes is a measure of the hydrogen or deuterium held on the surface and in turn a measure of the number of surface palladium atoms. Obviously, we have also assumed that the pretreatment conditions given in Table 2 adequately prepared the palladium surface for the experiments which followed. No assumptions about particle shape or site density for the palladium are needed.

By contrast, to obtain particle size from dispersion, special assumptions must be made concerning particle size distribution, particle shape, surface density of atoms as determined by the type and extent of crystallographic planes exposed and the average fraction of the surface of the particles accessible to the method of determining the number of surface atoms N_s. For instance, to obtain an average particle size for platinum supported on alumina, it has been assumed in certain studies (*18*) that the particles were cubes of uniform size with five faces accessible to the titrating gas used to determine N_s, each face having a surface density corresponding to the arithmetic average of those found on the low index planes (111), (110), (100).

Clearly, these assumptions were made only for the sake of convenience, and they are all open to criticism. As more methods become available to measure the dispersion D for more metals and alloys, it becomes important to agree upon a simple and, if possible, universal way to obtain particle size d from experimental values of D. The main reason is that a value of d is more easily grasped than value of D. But for the purposes of the present work, we have followed the prescription found in former work and obtained D from d as given by X-rays by the formula $D = 0.9/d$ (with d in nm).

From Eqs. (1) through (4) and the fact that the catalyst contained nominally 5% by weight of palladium, the values of dispersion in the last column of Table 3 have been calculated. The striking thing about all values obtained from chemisorption is that they are all essentially the same and in good agreement with those obtained from X-ray line broadening. One would expect that a *gross* error in *one* of these assumptions would show up as an anomalously high or low dispersion in Table 3. For example, if the oxygen-to-surface palladium ratio were far from unity [Eq. (1)], the dispersion determined by oxygen adsorption would be low relative to the dispersion determined by CO adsorption or the back-sorption technique. This in turn would cause the dispersion calculated from the titration uptake [Eq. (3)] to be low also. Because the various sorption techniques give practically the same dispersion, we conclude that this is not the case.

The assumption that the desorption of hydrogen is essentially complete at 653 K by pumping for 2 hr was confirmed by Expts 3 and 4. Extending the pumping time from 2 to 14.5 hr at 653 K did not decrease the subsequent adsorption of oxygen, as would have happened if hydrogen had not been removed. Any remaining hydrogen would have reacted with oxygen. In fact, the uptake was identical in both cases. As discussed in the Experimental Methods section we did not observe any significant remaining β-phase after pumping for 12 min at room temperature. This observation is supported by the work of

Rennard and Kokes (*18*), who showed that, for a palladium sponge with particles much larger than ours, dissolved hydrogen could be completely removed from a hydride having the composition $PdH_{0.23}$ by pumping at room temperature for 1 hr. From this we conclude that the backsorption technique and the oxygen-reverse titration were capable of measuring the dispersion. This is further supported by the fact that these techniques gave dispersion in agreement with the other techniques.

We wish to emphasize that we did not attempt an experimental check of the stoichiometries represented by Eqs. (1) through (4) and that it is possible that we did not attain monolayer coverage of hydrogen, deuterium, oxygen and carbon monoxide. Brennan, Hayward and Trapnell (*19*) report that on a palladium film the adsorption of oxygen at room temperature proceeds to 74% of a monolayer. Aben (*9*) has shown that at 343 K and a hydrogen pressure of 0.133 kPa palladium black is covered with a monolayer of hydrogen. On the other hand, Sermon (*12*) reports surface areas of palladium black measured by extrapolation of hydrogen uptake. The surface area measured in this way at 363 K was smaller than that measured subsequently at 273 K by a factor of 0.84. Values of dispersion listed in Table 3 would not be changed significantly by correction factors of this magnitude reflecting more precise stoichiometries. They would still be in good agreement between each other.

CONCLUSIONS

Since the titrations with hydrogen and deuterium at 100°C give essentially the same dispersion as the other methods we used, we conclude that the titration method assesses the dispersion adequately in spite of uncertainty about the exact adsorption stoichiometries involved and their change with particle size as size goes down (*20*), a situation common to all adsorption methods.

Of all the methods used, the titration is the most sensitive probe for surface palladium because approximately three hydrogen atoms are consumed for each surface palladium atom. All the other methods, including direct hydrogen adsorption at 100°C which was not performed by us, are much less sensitive. As we have already pointed out, there is evidence that carbon monoxide adsorbs in both the linear and bridged forms. The hydrogen back-sorption method becomes unreliable for poor dispersions since it involves taking the difference of two large numbers; in fact, the agreement of this method with the others in Table 3 is somewhat surprising.

Titrations with deuterium are more convenient to perform than ones with hydrogen since the β-phase hydride forms only at pressures above 1 atm; there is consequently much less danger of forming this hydride.

A further advantage of the titration method is that it can be used on reduced catalysts which have been exposed to air. There is no need to re-reduce and outgas the sample at high temperatures, a procedure which might alter the dispersion just before the surface area measurement is made (*21*). The only pretreatment needed is a brief outgas at about 100°C to remove air from the adsorption chamber and enough water from the alumina support so that it scavenges water formed during the titration. Indeed, in principle it should be possible to do the titration on palladium catalysts on hydrophobic supports if they are mixed with a small amount of previously dried alumina, silica or molecular sieve.

Finally, it is interesting to note that the titration of a commercial platinum on alumina catalyst which was coked gave the same dispersion as a fresh sample of the same catalyst (*22*). The same may be true for palladium.

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