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Oxidation of Small Palladium Particles

While there are abundant data on the interaction of palladium with dihydrogen, its interaction with dioxygen in a temperature range of catalytic interest (300–700 K) is relatively unexplored. Boreskov (*1*) first pointed out that near 525 K, palladium films took up an amount of dioxygen equivalent to the formation of 30 monolayers of PdO on prolonged exposure to about 13 Pa of dioxygen. Secondly, X-ray diffraction of oxidized Pd powders of micrometer size revealed unusual patterns that could not be ascribed to the common form of PdO, which has the tetragonal structure (*2*). In a recent study of silica supported Pd, significant uptake of dioxygen around 473 K by unoxidized samples was also reported as part of a study by infrared absorption of adsorbed carbon monoxide on oxidized Pd (*3*).

From the free energy of formation of bulk PdO, the most common oxide of Pd, we know that it is stable with respect to the metal and dioxygen up to 900 K, around 10 to 100 kPa partial pressure of dioxygen. Therefore, whether $PdO_{(s)}$ will be formed from $Pd_{(s)}$ and $O_{2(g)}$ around 300–700 K is a kinetic problem (*4*). In addition, other oxides such as PdO_2 and Pd_2O_3 could also be formed at temperatures below 473 K (*4*). Hence, there are two related questions concerning the oxidation of Pd, first under what conditions does the oxidation occur and second what is the nature of the oxide formed. We report here some answers to these two questions, with the aim of contributing to the characterization of supported Pd catalysts.

The uptake of gases by samples of silica supported Pd of two different dispersions was measured by the volumetric method. The first sample (S1) containing 1.30 wt% Pd was prepared by impregnation of $Pd(NO_3)_2$ in aqueous solution onto silica gel (Davison, Grade 950). After drying in a vacuum oven, it was oxidized at 673 K for 3 hr and then reduced at 673 K for 3 hr by dihydrogen. Dioxygen was obtained from Matheson (Research Grade). It was further purified by passing through a molecular sieve trap at 195 K. Dihydrogen was purified by passing through a Pd thimble (Milton Roy). The second sample (S2) containing 1.40 wt% Pd on SiO_2 was prepared by cation exchange of $[Pd(NH_3)_4]Cl_2$ onto the same support as used for S1. This method has been described elsewhere (*5*). The dispersion of the metal in the reduced samples, as determined by the Benson–Hwang–Boudart titration (*6*) is 15.3 and 57.0%, respectively. The adsorption apparatus, which is a conventional high vacuum manifold with a high precision pressure gauge (Texas Instruments) has also been described elsewhere (*7*). The Pd content in each sample was determined by atomic absorption.

Data of dioxygen uptake at various temperatures were collected as described in the next paragraph. These data were then compared with results of other tests described below.

A reduced sample was evacuated at 673 K for 2 hr to remove chemisorbed hydrogen. Then it was cooled down *in vacuo* to the adsorption temperature. It was equilibrated at that temperature for at least 1 hr. Dioxygen was then introduced to the sample chamber so that the resulting pressure was 6–10 kPa. The temperature was kept con-

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stant for 2 hr before the sample was cooled down to room temperature. An adsorption isotherm was recorded. The amount of dioxygen taken up was determined by extrapolation to zero pressure. The sample was then regenerated by reduction in static dihydrogen at 50 kPa, and 673 K, for 2 hr before the next adsorption.

In order to test whether the dioxygen taken up forms a stable compound the sample must be evacuated at the temperature of the uptake. Since other oxides of Pd such as PdO_2 and Pd_2O_3 are known to decompose to PdO and O_2 at 473 and 273 K, respectively (*4*), a comparison between the dioxygen uptake before and after evacuation could give information about the nature of the oxide formed, i.e., whether it is PdO, Pd_2O_3 or PdO_2. This information could be obtained by a relatively simple method which also verified that the metal retained its dispersion after each oxidizing uptake. The complete experimental sequence, carried on S1, is summarized in Fig. 1. In the first series of experiments, the first step was dioxygen uptake as described previously. Secondly, the sample was evacuated at room temperature for 1 hr. Dihydrogen was then introduced. After 2 hr of equilibration, an isotherm was obtained. Third, the amount of dissolved hydrogen was determined by the method of backsorption, i.e., the sample was evacuated at room temperature for 0.5 hr and another isotherm was obtained (*6*). The difference between the total uptake and the amount backsorbed was taken as the amount of hydrogen used to titrate the chemisorbed oxygen on Pd, to adsorb on the surface Pd and to react with oxygen taken up in the bulk. Then, the sample was re-reduced at 673 K under a static pressure of 50 kPa of dihydrogen. In the second series of experiments, after the evacuated sample was allowed to contact dioxygen at 6–10 kPa for 2 hr, without cooling, the sample was evacuated at the adsorption temperature for 1 hr. Then it was cooled *in vacuo* to room temperature. The hydrogen titration and backsorption was then carried out as in the first series of experiments. Finally, the sample was re-reduced for the next adsorption.

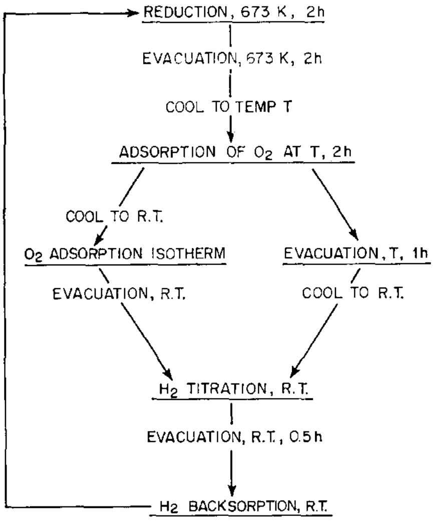

Fig. 1. A diagrammatical representation of the experimental sequence.

Figure 2a and b summarize the amount of dioxygen uptake, the dihydrogen reacted (total uptake minus amount backsorbed), as well as the amount backsorbed as a function of dioxygen adsorption temperature. Three facts emerge.

First, a marked increase in dioxygen uptake is observed around 538 K for both S1 and S2. Such a temperature is similar to that reported previously (*1–3*). The effect of such increase is much more pronounced for the sample with the lower dispersion as is reasonable. The uptake approaches a constant around 580 K for each sample. We will denote such an amount as the complete oxidation uptake. The ratio of the number of oxygen atoms calculated from the complete oxidation uptake to the total number of Pd atoms determined from atomic analysis, is very close to one (Table 1). This indicates that a form of palladium oxide, with an overall formula PdO, is being formed.

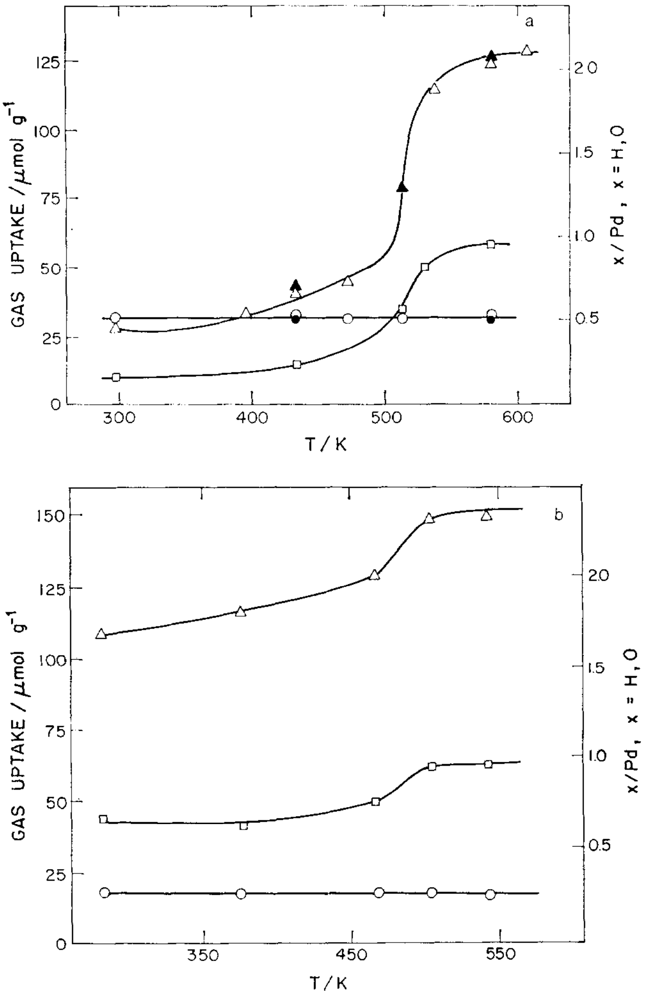

Fig. 2a. Gas uptake for S1; (b) gas uptake for S2. (□) O_2 taken up after adsorption at T; H_2 reacted, after oxygen adsorption; (△) (i) with evacuation at T; (▲) (ii) without evacuation at T; (⊙) H_2 backsorbed in (i); (●) H_2 backsorbed in (ii).

Second, concerning the amount of dihydrogen consumed by sample S1, column 2 of Table 2 shows that it is the same before and after high temperature evacuation. Thus, the oxide formed is stable with respect to evacuation at the uptake temperature. Hence, only the second series of treatments (that with high temperature evacuation was carried out on S2. Again, Fig. 2a and b show that the uptake of hydrogen closely parallels that of oxygen. The difference between the dihydrogen uptake after dioxygen adsorption at T and after that at room temperature is approximately twice the difference in dioxygen uptake at the same two temperatures (Table 2, columns 1, 2; 5, 6). Thus, the hydrogen titration reaffirms that significant bulk oxidation occurred around 538 K. Furthermore, the evacuation at high temperature guarantees that the oxide observed was formed at temperatures above 473 K and not during cooling. Since such temperatures do not favor the formation of PdO_2 or Pd_2O_3, the most likely oxide being formed is PdO.

TABLE 1

Comparison of Metal Dispersions Determined by Different Methods

	Properties	S1	S2
Pd	Pd content (μmol g^{-1})	122	131.(5)
O_2	Dioxygen uptake at room temperature (μmol g^{-1})	10.0	42.2
H_2 (tit)	Dihydrogen uptake at room temperature for titration (μmol g^{-1})	28.0	112.0
O_2 (c)	Complete oxidation uptake of dioxygen (μmol g^{-1})	58.0	61.2
D_1	$\frac{2 \times H_2\ (\mathrm{tit})}{3 \times \mathrm{Pd}} \times 100$ (%)	15.3	57.0
D_2	$\frac{2 \times O_2}{\mathrm{Pd}} \times 100$ (%)	16.4	64.2
D_3	$\frac{O_2}{O_2\ (\mathrm{c})} \times 100$ (%)	17.2	69.0

Third, the amounts of hydrogen *ab*sorbed remained constant after each treatment. Since the solubility of hydrogen in Pd depends on its dispersion as reported by Boudart and Hwang (*8*), we conclude that the dispersion of Pd remained constant during oxidation and reduction.

Finally, two samples were studied by X-ray diffraction. Due to the low metal loadings, the diffraction pattern of S1 was not very distinct after various treatments. Thus another sample, S3, prepared similar to S1, but with 4.0 wt% Pd, was also examined. After uptake of dioxygen on S1, S3 at 573 and 545 K, respectively, the samples were cooled to room temperature and exposed to air. Then, X-ray diffraction patterns were obtained. Each sample was then outgassed at room temperature for 0.5 hr and then exposed to dihydrogen for 2 hr (similar to a titration experiment). Another set of diffraction patterns was obtained in air. The first set of patterns, after the oxidative treatment, shows exclusively diffraction peaks of the normal form of PdO. Upon reaction with dihydrogen, the PdO peaks disappeared while distinctive Pd metal peaks were recorded. This is illustrated in Figs. 3a to d. Thus, the diffraction patterns again verified that PdO was formed

TABLE 2

Summary of Gas Uptake

Adsorption temp (K)	S1				S2			
	ΔO_2[a] (1)	ΔH_2[a] (2)	H_2(b)[b] (3)	Run (4)	ΔO_2[a] (5)	ΔH_2[a,c] (6)	H_2(b)[b] (7)	Run (8)
298	0.0	0.0	31.5	1	0.0	0.0	18.5	1
395	—	5.0	—	6	0.0	0.0	17.5	5
433	4.5	14.5	31.5	2	—	—	—	—
	—	13.5[c]	32.5	2	—	—	—	—
473	—	16.5	31.5	7	—	—	—	—
508	—	26.5	—	5	7.0	16.0	17.5	2
513	24.5	51.0[c]	31.5	9	—	—	—	—
538	40.0	77.0	—	4	19.0	36.0	18.0	3
580	48.0	98.0	32.0	3	19.0	36.0	16.5	4
	—	97.0[c]	32.5	3	—	—	—	—
606	—	101.0	—	8	—	—	—	—

[a] ΔX_2 = (gas uptake after O_2 adsorption at T) − (gas uptake after O_2 adsorption at room temp) in μmol g^{-1}; $X_2 = O_2, H_2$.

[b] H_2 backsorption in μmol g^{-1}.

[c] Determined with evacuation at oxidation temperature; all other data collected without evacuation at oxidation temperature.

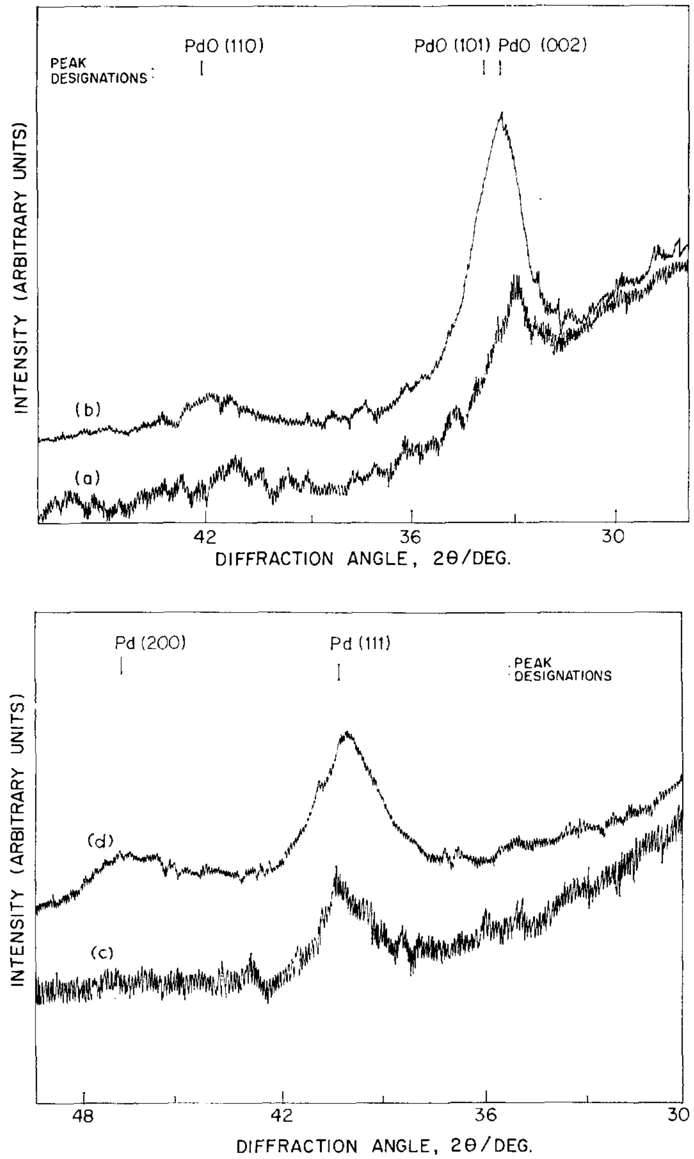

FIG. 3. X-Ray diffraction patterns. (a) S1 after adsorption of O_2 at 573 K; (b) S3 after adsorption of O_2 at 545 K; (c) oxidized S1 exposed to H_2, RT; (d) oxidized S3 exposed to H_2, RT.

upon moderate oxidation of supported Pd samples, and that the oxide formed could essentially be reduced by reacting with dihydrogen at room temperature.

Noteworthy is the ease of reduction of the oxide formed. The agreement between the increase in hydrogen uptake and twice the increase in oxygen uptake after the oxidative treatment at each temperature (relative to room temperature uptake), suggests that the majority of the oxide formed was re-reduced even at room temperature as also indicated by X-ray diffraction.

More importantly, the observation that particles of Pd of ca. 7 nm in average size or smaller can be completely oxidized to PdO around 538 to 580 K leads us to suggest a simple alternative method for determining the dispersion of Pd. Precisely, two gas uptakes have to be measured. First, the surface Pd atoms can be determined by oxygen adsorption at room temperature, for example. Second, the total Pd atoms can be deduced from the complete oxygen uptake on the reduced and evacuated Pd particles at 580 K. Note that on Pd which has oxygen preadsorbed at room temperature, dioxygen uptake appears to be very slow upon heating up from room temperature to 580 K. Table 1 shows that the dispersion of Pd in S1 and S2 determined by this method (D_3) agrees satisfactorily with the values calculated with the help of elemental analysis for Pd (D_1, D_2).

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Y. L. Lam
M. Boudart[1]

Department of Chemical Engineering
Stanford University
Stanford, California 94305

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[1] To whom correspondence should be sent.