

## NOTE

## Hydrogen/Oxygen Titration Method for Measurement of Pd Dispersion on Supported Catalysts

Palladium has long been recognized as an effective catalyst for many organic reactions in the liquid phase, especially when supported on carbon. To evaluate the qualities of the different types of catalysts available on the market, it is necessary to characterize them by measuring the free metal surface area, that is, the dispersions. It is well known that, using largely empirical recipes, the dispersion of some metals can be measured by chemisorption methods.

Hydrogen chemisorption is undoubtedly the most widely used method for the measurement of metal dispersion on supported catalysts. However, the result obtained by this method on supported palladium catalysts can sometimes be inaccurate because of hydride formation and sintering during the pretreatment at high temperature (1). The extent of the sintering of supported palladium particles depends on the properties of the supports. Since the strengths of metal-support interactions involving alumina are generally stronger than those involving carbon, the sintering is much more extensive on carbon supports than on alumina. As evidence, Fig. 1 indicates that the high temperature evacuation before chemisorption may induce significant sintering of finely dispersed palladium particles on carbon supports.

In order to obtain the chemisorption measurements, Pd/C catalysts require the mildest possible pretreatment, and indeed, it may not be possible to clean the surface without sintering the metal. In this respect, the oxygen–hydrogen titration method which was originally developed for supported platinum (2) has a distinct advantage over the other chemisorption methods. It was possible to use the hydrogen titration without the formation of the Pd–hydride only by employing the modification of raising the temperature to 373 K (3, 4).

The oxygen–hydrogen titration method can be used on reduced catalysts which have been exposed to air. There is no need to rereduce and outgas the sample at high temperature, a procedure which might alter the dispersion just before the surface area measurement is made as discussed earlier. The only pretreatment needed is a brief outgas at about 100°C to remove air from the adsorption chamber and water from the support. However, the authors observed that this technique sometimes gives erro-

neous results, especially for the catalyst samples exposed to air for an extended period.

Figure 2 shows that, after the first oxygen–hydrogen titration cycle had been carried out, there were reproducible results in subsequent oxygen–hydrogen titrations. In some cases, even three or four oxygen–hydrogen titration cycles (OHTC) were required to obtain reproducible results. It looks as if the fresh catalyst surface is in metastable condition which is smoothed out after one or more titrations thereby producing a more “homogeneous” surface. The reason for this should necessarily be in the complexity of the interaction of hydrogen and oxygen with irreproducible fresh catalyst surfaces. The large amount of the first hydrogen titration uptake on carbon-supported Pd catalyst may be related to the surface oxygen groups on the carbon support (5).

One problem observed when carrying out the oxygen–hydrogen titration cycles was related to a slow uptake of oxygen during the hydrogen–oxygen titration. The first dose of oxygen admitted to the system as well as successive ones did not reach equilibrium in a few hours. Also a correction for oxygen adsorbed on the support was needed. In the oxygen–hydrogen titration cycles, the exposure to air at room temperature for 16 h had been used for generating an oxygen-covered surface instead of the normal oxygen titration procedure. That is, the oxygen–hydrogen titration cycles were the repeated hydrogen titrations of surface oxygen formed by exposure to air until a constant titration value was obtained.

The OHTC can be successfully used in characterizing the dispersion of unreduced Pd/C catalysts. The catalyst samples may be reduced during one or more titrations, that is, in static hydrogen atmosphere at 100°C. Therefore, the oxygen–hydrogen titration cycles method can be recommended for the routine determination of the dispersions of supported palladium metals. As reported in Table 1, OHTC results are in good agreement with dispersions from XRD and TEM.

As shown in Fig. 2, the hydrogen titration isotherms for Pd/C show two hydrogen uptake processes: one at low hydrogen pressure and the other at pressures higher than about 250 Torr. The first comes from hydrogen titration on surface oxygen, and the second may be assigned

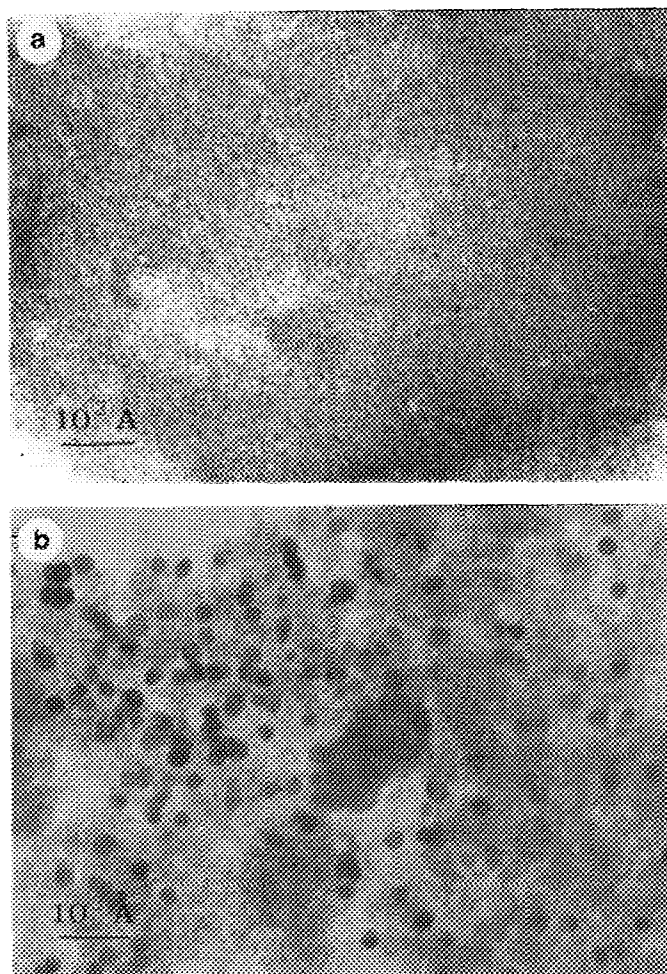


FIG. 1. TEM view of commercial Pd/activated carbon supplied from Engelhard; (a) before and (b) after evacuation at 400°C for 16 h.

to hydrogen absorption. The transition pressure was found to be quite variable, depending upon the palladium dispersion, characteristics of carbon support, etc. The amounts of monolayer titrations were determined by extrapolating the linear portion of the low pressure region to zero pressure.

Flow techniques and gas chromatography offer an alternative to the static volumetric or gravimetric chemisorption measurements (6). The advantages here are the simplicity, the speed, and repeatability of the measurements. The disadvantage of this technique is that the catalyst may not be able to hold weakly or reversibly chemisorbed gas and this may lead to desorption and low dispersion results.

The pulse technique is derived from the flow technique. For the present study, the Benson–Boudart gas titration of palladium surfaces has been adapted to the quicker gas-chromatographic pulse technique. This technique cannot

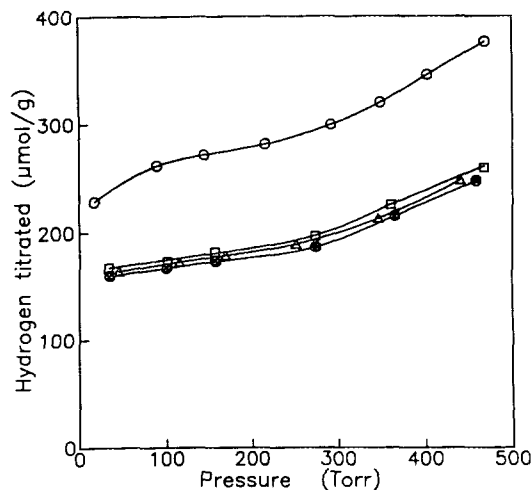


FIG. 2. Oxygen–hydrogen titration isotherms during the OHTC: (○) the first cycle, (●) the second cycle, (□) the third cycle, and (△) the fourth cycle.

be employed for chemisorption of hydrogen and oxygen on Pd/C catalysts due to sintering during pretreatment at high temperature for chemisorption.

In the case of hydrogen titration at 100°C, eluted pulses showed pronounced tailing which led to gradual upward baseline drift. This problem was also observed at 200°C, –78°C, and room temperature. However, hydrogen pulses after passage through a sample of carbon alone showed no tailing. Hence, even at –78°C, a part of the

TABLE 1  
Comparison of Average Crystallite Diameters Obtained by Various Methods

Catalyst code	Type of diameter <sup>a</sup>	Average crystallite diameter (Å)		
		TEM	XRD	OHTC <sup>c</sup>
EU (4.05% Pd) <sup>b</sup>	$d_n$	32	—	—
	$d_s$	39	—	40
	$d_v$	43	38	—
SA-IA (4.75% Pd) <sup>c</sup>	$d_s$	29	—	26
VB-AP (4.67% Pd) <sup>d</sup>	$d_s$	—	—	53
	$d_v$	—	60	—

<sup>a</sup>  $d_n$ , number average ( $\sum n_i d_i / \sum n_i$ );  $d_s$ , surface average ( $\sum n_i d_i^3 / \sum n_i d_i^2$ );  $d_v$ , volume average ( $\sum n_i d_i^4 / \sum n_i d_i^3$ ).

<sup>b</sup> Commercial Pd/activated carbon catalyst from Engelhard.

<sup>c</sup> Prepared by Impregnation by Adsorption (IA); activated carbon support from Strem Chemicals.

<sup>d</sup> Prepared by adsorption and precipitation (AP); carbon black support (Vulcan 3) from Cabot Corp.

<sup>e</sup> Titration stoichiometry used to calculate average diameters: Pd–O + (3/2)H<sub>2</sub> → Pd–H + H<sub>2</sub>O.

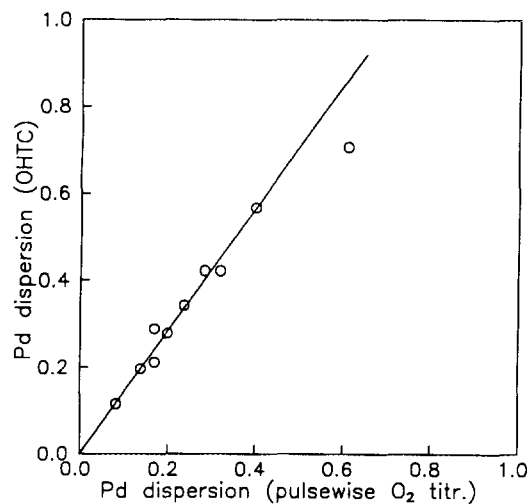


FIG. 3. Comparison between the OHTC and the pulsewise oxygen titration.

hydrogen has a substantial residence time on the palladium due to a weak, reversible form of adsorption. In addition to integration errors of the eluted peaks due to the shape of these peaks and baseline drift, the chemisorbed quantity estimated by the pulsewise hydrogen titration may be significantly affected by intervals between the pulses injected.

Oxygen was also chemisorbed rapidly at room temperature and no reversible adsorption occurred. Pulses eluted on completion of the oxygen monolayer were almost identical to those obtained with carbon support alone. As a result, oxygen titration could be measured more rapidly and more accurately than that of hydrogen, and oxygen was a particularly suitable adsorbate for use with the pulse method.

For various carbon-supported Pd catalysts, comparison of data from the pulsewise oxygen titration method and the static volumetric hydrogen titration cycles (OHTC)

is given in Fig. 3. Both methods were found to be in fair agreement, but the palladium dispersions estimated by the pulse method were generally less than those from volumetric methods as expected.

In summary, by examination and modification of some titration techniques the OHTC and pulsewise oxygen titrations were found to be reliable experimental techniques when palladium dispersion needs to be measured routinely.

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