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RESEARCH NOTE

A Rapid Method for the Evaluation of the Dispersion of Palladium in Supported Catalysts

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In the literature many techniques have been proposed for the evaluation of the specific metal surface area in supported catalysts. In particular, we are aware of methods based on the measurement of the chemisorbed hydrogen uptake (1, 2), the carbon monoxide uptake (1, 3, 4), the X-ray line-broadening technique (5, 6), electron microscopy (7), H_2/O_2 titration (8), and the hydrogen pulse technique (9, 10). Many of these methods are reviewed by Ragaini *et al*. (11).

The methods based on hydrogen chemisorption normally require prolonged treatments of the prereduced catalysts at relatively high temperatures (450–500°C) for a long time (3–16 h) under vacuum or by using an inert gas stream, in order to remove all the chemisorbed hydrogen and to clean the surface completely. Such conditions may cause sintering (2, 9, 10), especially when dealing with highly dispersed catalysts, accompanied by loss of accuracy. Methods based on the titration of chemisorbed oxygen with hydrogen have same drawbacks including the spillover of oxygen and the long time necessary for completing the measurement (12).

In this note we present a fast and simple method to evaluate the palladium surface area in supported catalysts, which is particularly useful for highly dispersed catalysts, as it can be performed under relatively mild temperature conditions. The method is an extension of one proposed previously by Hoeg Van *et al*. (13) for platinum-supported catalysts.

By comparing it with other techniques the method appeared to be reliable and reproducible when repeated many times with the same sample.

The apparatus is very simple and consists of a cylindrical reactor of 1.25 cm of internal diameter, containing the powdered catalyst (0.5–1 g). The reactor is placed in the oven of a gas-chromatograph and connected with a six-way sampling valve with a loop of known volume. The reactor and valve are connected to the TCD detector of the gas-chromatograph.

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Initially the catalysts were prereduced at 300°C for 2 h in a stream of hydrogen of 50 cm^3/min, then cooled down to 150°C in a stream of pure nitrogen (30 cm^3/min) and treated, at the same temperature, with 5–10 pulses of oxygen of about 0.15 cm^3 volume. By operating under these conditions, we have found that oxygen selectively reacts with chemisorbed hydrogen according to the reaction

$$2\,Pd_s{-}H + \tfrac{1}{2}O_2 \rightarrow 2\,Pd_s + H_2O \qquad [1]$$

in which Pd_s is a palladium surface site. The reaction,

$$Pd_s + \tfrac{1}{2}O_2 \rightarrow Pd_sO, \qquad [2]$$

is comparatively slow and does not occur significantly, as a consequence of both the low oxygen residence time and the relatively low temperature. Next the surface, cleaned of the adsorbed hydrogen, is submitted to a number of hydrogen pulses of the same volume as used in oxygen pulsing (0.15 cm^3) at 150°C. We obtain chromatograms similar to the one reported in Fig. 1. From these chromatograms the amount of chemisorbed hydrogen can be calculated from the relationship:

$$V_{\text{hydrogen}} = V_{\text{loop}} \sum_{i=1,n} [1 - (A_i/A_0)]. \qquad [3]$$

From the amount of chemisorbed hydrogen we can calculate the palladium-specific surface area, the metallic dispersion, and the mean crystallite size in the usual way, assuming a surface stoichiometry ratio $H/Pd_s = 1$ and a palladium surface site density of 1.2×10^{19} sites/m^2, in agreement with the suggestions of Aben (2).

It must be pointed out that the conditions used have been chosen in order to avoid any possibility of β-hydride phase formation during the pretreatments and measurements, in agreement with the findings reported by Aben (2) and Joyal and Butt (10).

In Table 1 we report the results obtained for three catalysts with different metal dispersions and supports.

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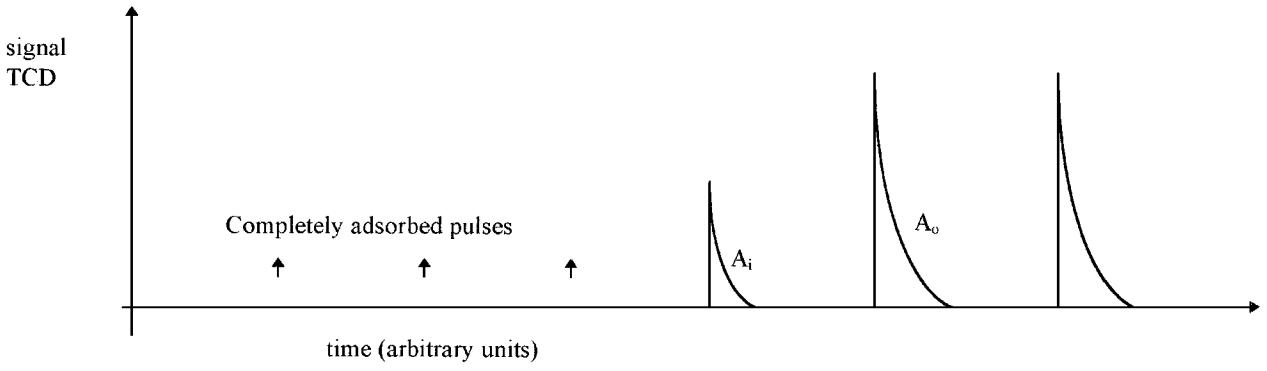

FIG. 1. An example of the chromatogram obtained by submitting a catalyst to pulses of hydrogen at 150°C. The duration time of each emerging pulse is in the range 40–80 s, according to the amount of catalyst charged in the reactor (0.5–1.0 g).

These catalysts were prepared by using different techniques such as ionic exchange (14, 15) and ligand exchange (16, 17).

The results presented in Table 1 were independent of the number of oxygen pulses, which number exceeded that necessary to reach stoichiometry. The results were also independent of the time span between successive pulses. On the other hand, if a stream of oxygen is fed to the reactor (30 cm^3/min) for 30 or more minutes at 150°C, the volume of the hydrogen uptake in the pulse titration increased by a factor of three. This fact suggests that, as to be expected, a prolonged treatment of the surface with oxygen results in oxygen chemisorption. This fact, confirms that the adopted procedure, characterized by a low residence time of the oxygen pulses above the catalyst has the effect of cleaning the surface without reacting to give Pd_sO. In order to verify this we also compared the results obtained for catalyst C1, reported in Table 1, with those obtained for the same catalyst with carbon monoxide chemisorption in a static apparatus (6). Under standard conditions, we obtained an amount of carbon monoxide adsorption of about 1.05 cm^3/g of catalyst, corresponding to a metallic dispersion of about 0.35, assuming an adsorption stoichiometry Pd/CO of 1.4 (3). This results in a satisfactory agreement with the data reported in Table 1 for this catalyst.

Catalysts C2 and C3 have also been examined by measuring the X-ray line broadening. For catalyst C2 we obtained a mean diameter of the crystallites of about 2.7 nm, in agreement with the data in Table 1. For catalyst C3 we did not observe any difference in the XRD spectrum of the catalyst and the support; it follows that for this catalyst, the metal particles have diameters less than 1.5 nm (5), in agreement with the data in Table 1.

Finally, we examined the effect of cleaning the catalyst surface by flushing in a stream of inert gas at high temperature (500°C) for a prolonged time (3–16 h) as described in the literature (8, 9, 13). For this purpose we have submitted catalysts C1 and C3 to two different treatments: (i) reduction at 300°C in a hydrogen stream for 2 h, flushing at 500°C with nitrogen (30 cm^3/min) for 3 h, cooling to 150°C and titration of the surface palladium atoms with hydrogen pulses (D′); (ii) reduction under the same conditions mentioned previously, elimination of chemisorbed hydrogen with oxygen pulses at 150°C, and determination of the metallic dispersion with pulses of hydrogen at the same temperature (D″).

The results obtained are summarized in Table 2. As can be seen the two methods of cleaning the surface gave nearly the same result, but comparing these results with those reported in Table 1 shows that the highly dispersed catalyst C3 gives, after the high temperature treatment, a dispersion value of 0.50, instead of 0.90, whereas the result remains unchanged for the C1 catalyst. It follows that, the high-temperature treatment has a strong influence on the metal surface area only in the case of catalysts with a very high metallic dispersion.

In conclusion, the proposed method described in this note gives reliable and reproducible results in a short time, using a cheap and very simple apparatus.

TABLE 1

Values of Metallic Dispersion Obtained for Three Different Catalysts Submitted to Pulses of Hydrogen

Catalyst	Description	Dispersion (D)	S_{Pd} (m^2/g_{Pd})	d_p (nm)
C1	2 wt% Pd/silica-alumina	0.36	170	2.7
C2	0.5 wt% Pd/silica	0.45	191	2.6
C3	0.5 wt% Pd/γ-alumina	0.90	424	1.2

TABLE 2

Values of Metallic Dispersion Obtained for C1 and C3 Catalysts Submitted to Two Different Treatments (see Text for Details)

Catalysts	D′	D″
C1	0.33	0.31
C3	0.50	0.46

Notation

$V_{hydrogen}$ = volume of adsorbed hydrogen, cm^3
V_{loop} = volume of loop of six-way sampling valve, cm^3
A_i = peak area of the hydrogen i-th pulse with adsorption
A_0 = peak area of the hydrogen pulse without adsorption
S_{Pd} = specific area of metal, m^2/g_{Pd}
d_p = mean diameter of crystallites, nm
D' = dispersion found after the first type (i) of surface cleaning
D'' = dispersion found after the second type (ii) of surface cleaning

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