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Note

Pulse technique for the chromatographic determination of metal dispersions in palladium catalysts

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For the determination of palladium dispersions, with or without various supports, oxygen, carbon monoxide and hydrogen have been used as adsorbates in chemisorption methods[1–12]. In these methods, static high-vacuum systems are commonly used.

Recently, there has been increasing interest in pulse flow techniques for the rapid determination of fast and irreversible adsorption on metal surfaces. The most frequently used technique for the determination of palladium dispersions consists of adsorption on "clean" surfaces. Benson *et al.*[11] recently used oxygen–hydrogen titration, under static conditions, for determining the dispersion of palladium on aluminium oxide. According to Buianova *et al.*[7,8], oxygen is most useful as an adsorbate in palladium surface area determinations. Because of the well known solubility of hydrogen in palladium, hydrogen can be used for palladium surface area determinations only under carefully controlled conditions[9–12] in which the amount of absorbed hydrogen is negligible in comparison with the amount of hydrogen chemisorbed on the palladium surface. The pulse dynamic method, developed by Gruber[13] and modified by Roca *et al.*[14] and Freel[15], has so far been used mainly for chemisorption determinations with platinum.

EXPERIMENTAL

The experiments were carried out with the system shown in Fig. 1. Argon containing 8% nitrogen was used as the carrier gas at a flow-rate of 40 ml/min. Trace amounts of oxygen were removed from the carrier gas at 180° in the glass column containing a copper catalyst supported on γ-alumina. In order to remove water vapour, a column containing molecular sieve 5A was used. The efficiency of removal of oxygen was checked indirectly by the independence of the amount of oxygen sorbed by the "clean" catalyst surfaces on the time of passage of carrier gas.

Oxygen and hydrogen produced electrolytically and purified over palladium–γ-alumina catalyst were used as the adsorbates. Trace amounts of water vapour were removed in the column containing molecular sieve 5A. Oxygen or hydrogen was introduced through the four-way valve, calibrated with mercury with an accuracy of 2%. The volume of gas introduced was 0.139 or 0.0689 ml. A katharometer was used as the detector.

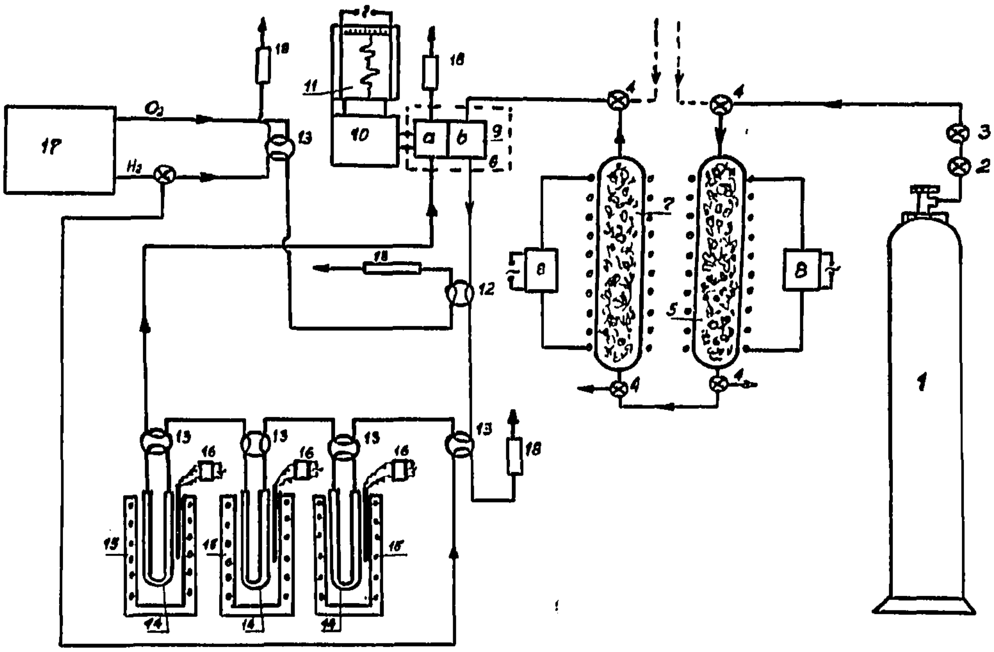

Fig. 1. Experimental system for determination of chemisorption under dynamic conditions. 1 = Bottle containing carrier gas; 2 = reducing valve; 3 = control valve; 4 = three-way stopcocks; 5 = column containing Cu-γ-Al$_2$O$_3$ catalyst; 6 = thermostat; 7 = column containing molecular sieve 5A; 8 = transformers; 9a and b = katharometers; 10 = supplier for katharometer; 11 = recorder; 12 = four-way sampling stopcock; 13 = four-way stopcocks; 14 = U-tubes containing catalyst; 15 = electric furnaces; 16 = thermoregulators; 17 = electrolyzer and system for oxygen and hydrogen purification; 18 = flow-meters.

Samples of catalysts (1.5–3.0 g) were placed in a Pyrex U-tube of height 20 cm and I.D. 3 mm. The support for the catalysts was γ-alumina with a specific surface area and porosity structure determined by adsorption of argon in the standard vacuum apparatus. The specific surface area was 200 m^2/g and the dominant pore radius was 25 Å. Palladium(II) chloride was sorbed on the support from solutions of various concentrations; the sorption time was 3 days. The catalysts were then separated, rinsed with distilled water, dried at 110° and reduced with electrolytic hydrogen for 6 h at 300°. The amount of palladium sorbed was determined by solution analysis. By this means, catalysts containing 0.1–0.4% (w/w) of palladium were prepared. When a catalyst sample was placed in the U-tube, carrier gas was passed over it at 300° for 2 h and then the catalyst was reduced at 270° with electrolytic hydrogen passed for 2 h at a flow-rate of 20 ml/min. After catalyst reduction, hydrogen was removed by passing the carrier gas at 300° for 2 h. The sample was subsequently cooled to ambient temperature in a stream of carrier gas. We have assumed that catalysts prepared in this manner had a "clean" surface. Of was used for the determination of oxygen or hydrogen chemisorption at ambient temperature.

RESULTS

The chemisorption was determined by introducing pulses of oxygen or hydrogen into the stream of carrier gas until a constant height of the recorded peaks

TABLE I

CHEMISORPTION OF OXYGEN AND HYDROGEN ON PALLADIUM–γ-ALUMINA CATALYSTS

$V_O{}^c$ = volume of oxygen chemisorbed on "clean" surface of catalyst at 25° (reaction 1).
$V_O{}^r$ = volume of oxygen consumed in reaction with reduced catalyst surface at 25° (reaction 4).
$V_H{}^c$ = volume of hydrogen sorbed on "clean" surface of catalyst at 25° (reaction 2).
$V_H{}^{\circ}$ = volume of hydrogen consumed in reaction with oxidized catalyst surface at 25° (reaction 3).
$V_O{}^{r(120^\circ)}$ = volume of oxygen consumed in reaction with reduced catalyst surface at 25° (reaction 4).
$V_H{}^{c(120^\circ)}$ = volume of hydrogen chemisorbed at 120°, equal to 2 $(V_O{}^{r(120^\circ)} - V_O{}^c)$.
$V_H{}^{ir}$ = volume of hydrogen reversibly bound to catalyst, equal to $V_H{}^c - V_H{}^{c(120^\circ)}$.
H:O = ratio of volume of hydrogen to volume of chemisorbed oxygen (reaction 3), equal to $(V_H{}^{\circ} - V_H{}^{ir})/V_O{}^c$.
O:H = ratio of volume of oxygen to volume of chemisorbed hydrogen (reaction 4), equal to $(V_O{}^{r0} - \frac{1}{2} V_H{}^{ir})/V_H{}^{c(120^\circ)}$.

Pd content (%, w/w)	$V_O{}^c$ *(ml/g of catalyst)*	$V_O{}^r$ *(ml/g of catalyst)*	$V_H{}^c$ *(ml/g of catalyst)*	$V_H{}^{\circ}$ *(ml/g of catalyst)*	$V_O{}^{r(120^\circ)}$ *(ml/g of catalyst)*	$V_H{}^{c(120^\circ)}$ *(ml/g of catalyst)*	$V_H{}^{ir}$ *(ml/g of catalyst)*	*H:O*	*O:H*
0.86	0.112	0.362	0.466	0.730	0.173	0.122	0.344	3.44	1.56
1.05	0.181	0.450	0.483	0.875	0.273	0.184	0.299	3.18	1.64
1.37	0.200	0.520	0.600	1.029	0.293	0.186	0.414	3.08	1.68
1.82	0.232	0.985	1.540	2.030	0.346	0.225	1.315	3.08	1.50
4.21	0.397	1.040	1.390	2.270	0.582	0.370	1.020	3.15	1.45

was achieved. Also, the oxygen adsorbed on the catalyst was titrated with hydrogen (*cf.*, reaction 3), and the hydrogen adsorbed on the catalyst was titrated with oxygen (*cf.*, reaction 4). The results obtained are summarized in Table I.

No evidence for the sorption of oxygen or hydrogen on the γ-alumina support was found under the conditions used.

Because it is difficult to remove hydrogen dissolved in palladium at ambient temperature, a special procedure was used in order to eliminate the effect of absorbed hydrogen and to determine the amount of irreversibly sorbed hydrogen. After catalyst

TABLE II

RESULTS FOR THE DETERMINATION OF THE SPECIFIC SURFACE AREA OF PALLADIUM

$\frac{S_O - S_H}{S_O}$ = difference between the results obtained with the use of oxygen and hydrogen.
$\frac{S_O{}^s - S_O{}^d}{S_O{}^s}$ = difference between the results obtained by the static and dynamic method with the use of oxygen.

Pd content (%, w/w)	*O:Pd*	S_O *(m²/g Pd)*	*H:Pd*	S_H *(m²/g)*	$\frac{S_O - S_H}{S_O}$ *(%)*	$\frac{S_O{}^s - S_O{}^d}{S_O{}^s}$ *(%)*
0.32	0.210	93.6	0.196	89.4	+ 4.5	+ 3.6
0.86	0.147	69.3	0.149	70.4	− 1.5	− 3.5
1.00	0.133	62.4	0.130	61.2	+ 2.0	—
1.37	0.125	58.7	0.116	54.6	+ 6.7	—
1.82	0.109	51.3	0.105	49.7	+ 3.0	—
4.21	0.081	37.9	0.075	35.3	+ 6.9	—

reduction, hydrogen was removed by passing a stream of carrier gas for 2 h at 120°, the sample was cooled to ambient temperature and the remaining hydrogen titrated with oxygen. The results obtained are given in Table I (column 6). The obtained results for titration with oxygen at 120° were insignificantly (less than 10%) higher than those obtained at ambient temperature.

Table II gives the results of dispersion determinations for palladium–γ-alumina catalysts obtained from chemisorption of oxygen on the "clean" metal surface at ambient temperature and from chemisorption of hydrogen at 120° estimated by titration with oxygen.

DISCUSSION

The chemisorption processes and the titrations can be described as follows:

$$Pd_S + {}^1/_2\,O_2 \rightarrow Pd_SO; \qquad O{:}Pd_S = 1 \tag{1}$$

$$Pd_S + {}^1/_2\,H_2 \rightarrow Pd_SH; \qquad H{:}Pd_S = 1 \tag{2}$$

$$Pd_SO + {}^3/_2\,H_2 \rightarrow Pd_SH + H_2O; \qquad H{:}O = 3 \tag{3}$$

$$Pd_SH + {}^3/_4\,O_2 \rightarrow Pd_SO + {}^1/_2\,H_2O; \qquad O{:}H = 1.5 \tag{4}$$

where Pd_s denotes a palladium atom on the catalyst surface.

On comparing the sorption of oxygen (Table I, column 2) with that of hydrogen (column 4), it is found that the latter is greater, owing to the significant absorption of hydrogen in palladium. This is shown by the increase in the difference between the sorption of oxygen and that of hydrogen with increase in palladium content; the solubility of hydrogen is greater in large crystallites of palladium.

We attempted to remove the loosely bound hydrogen from palladium at ambient temperature. Although a significant decrease in the amount of sorbed hydrogen was observed, the procedure was too time consuming to be practical. The results obtained by titration (Table I, columns 3 and 5) cannot be interpreted quantitatively under these conditions because of the uncontrolled absorption of hydrogen in palladium. The amount of chemisorbed hydrogen was therefore determined indirectly by titration with oxygen (Table I, column 6).

It was found that a period of 2 h at 120° is sufficient to remove the reversibly bound hydrogen. No evidence for further removal was found by titration with oxygen at ambient temperature. If, from the results obtained by titration with oxygen (column 6), one subtracts the amounts of oxygen chemisorbed on the "clean" surface (column 2), one obtains the amounts needed for hydrogen titration. Taking into account the stoichiometry for the formation of water (O:H = 1:2), one obtains the results in column 7, corresponding to the amounts of irreversibly bound hydrogen at 120°.

The amounts of reversibly bound hydrogen (column 8) were obtained as the differences between the values in columns 4 and 7. On comparing these results with the palladium content, it is found that the amount of reversibly sorbed hydrogen increases with palladium content, as expected.

The results for the reversible sorption of hydrogen were used in order to check the procedure. From the results in Table I, the H:O ratio for reaction 3 and the O:H ratio for reaction 4 were determined (columns 9 and 10). Reasonable agreement between these values and those predicted is evident. Some differences may be attributed to the inaccuracy of the determination of the reversible sorption of hydrogen, which is not easy to control under dynamic conditions.

Table II gives results for the chemisorption of oxygen and hydrogen and also the surface area and dispersion of palladium in the catalysts. Differences between the results obtained from chemisorption of oxygen on the "clean" surfaces and the results obtained by titration of the irreversibly bound hydrogen are also given. Reasonable agreement of the results is evident.

In the last column in Table II there is given a comparison, for two catalyst samples, of the results for the chemisorption of oxygen on "clean" surfaces obtained under static and dynamic conditions. Taking into account the specific features of both methods, there is good agreement between the results.

There may be some objections to the comparison of chemisorption of oxygen at 25° with chemisorption of hydrogen at 120°. Regardless of the uncertain stoichiometry of the chemisorption of oxygen and hydrogen (reactions 1 and 2), which has been the subject of numerous investigations[6,7,9,10], one must assume that this stoichiometry is the same at 120° and ambient temperature. This is also indicated by the fact that the isotherms for the chemisorption of hydrogen on palladium black in this temperature range[12] suggested constant stoichiometry. From the results, it follows that even at low pressures (down to 4 mmHg), chemisorption of hydrogen is accompanied by absorption of hydrogen in palladium; an increase in temperature to 130° removes the absorption without any change in the chemisorption of hydrogen.

It can be concluded that the pulse chromatographic method for the determination of palladium dispersion with oxygen and hydrogen as adsorbates is useful, despite the difficulties in the determination of the chemisorption of hydrogen and in the titration of the reduced surface with oxygen. It seems that titration with hydrogen, at higher temperatures, of the surface area of palladium oxidized at low temperatures enables one to determine the dispersion of supported palladium.

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