

CHROM. 10,822

GAS CHROMATOGRAPHY OF THE PALLADIUM-OXYGEN SYSTEM OVER A WIDE TEMPERATURE RANGE

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(First received October 5th, 1977; revised manuscript received December 14th, 1977)

SUMMARY

The interaction between oxygen and palladium supported on alumina and silica and between oxygen and palladium black was examined. Three different temperature ranges were found in the interaction between oxygen and palladium: range I (300–470°K) in which surface chemisorption of oxygen occurs, range II (470–770°K) in which oxygen chemisorption is followed by incorporation of oxygen into bulk metal and range III (above 770°K) in which complete oxidation of palladium catalysts to palladium monoxide occurs. Considering the possibility of the complete oxidation of palladium at 770°K, the quantitative determination of palladium in palladium-support catalysts was suggested by means of gas titration with hydrogen.

The possibility of carrying out the redispersion of palladium catalysts by oxidation was investigated.

INTRODUCTION

The interaction of oxygen with the surface of metals plays an important part in investigations of mechanisms of catalytic reactions, in corrosion processes and in determinations of the selective surface of metals¹. Many workers have dealt with interactions between oxygen and metals, but systematic studies of the palladium-oxygen system over a wide temperature range are lacking. Chemisorption of oxygen at room temperature on the surface of palladium occurs rapidly and irreversibly and is connected with the dissociation of oxygen molecules into atoms. It has been used in the determination of the selective surface of palladium, especially under dynamic conditions². In the literature there is no agreement as far as the stoichiometry of the interaction between oxygen and the surface atoms of palladium (Pd_s) is concerned.

According to Brennan *et al.*³, the O:Pd_s stoichiometry is 0.7, whereas Bujanova *et al.*² gave a value of 0.66. Assuming a stoichiometry of 1, Benson *et al.*⁴ obtained good agreement for the results of palladium dispersion as measured by sorption of oxygen and carbon monoxide, oxygen-hydrogen titration and X-ray diffraction line broadening.

Except for general statements about the possibility of forming non-stoichio-

metric bulk oxides, no data have been given concerning the behaviour of the palladium–oxygen system at higher temperatures, and this problem is the subject of this paper.

In the latest studies^{5–7} dealing with the interaction of carbon monoxide with palladium in the presence of oxygen, the above problem was considered only briefly, with attempts to explain changes in the rate of oxidation of carbon monoxide and changes in the energy of bonding of carbon monoxide with palladium on the basis of the interaction between palladium and oxygen.

EXPERIMENTAL

The investigations were carried out in a pulse chromatographic system described in detail earlier⁸. Argon was used as the carrier gas; its purification was outlined earlier⁸. The catalyst used, manganese(II) oxide supported on alumina, makes it possible to remove oxygen from the carrier gas to a residual level of less than 1 part in $10^{9.5}$ (ref. 9).

The sample of palladium catalyst or palladium black examined (0.2–0.5 g) was placed in a glass U-tube. Thermoconductive sensors in a bridge system were used as the measuring element, and their readings were recorded on a register. Pulses of oxygen or hydrogen were fed into the stream of carrier gas by means of a glass four-way valve or a metal six-way valve. Volumes of the samples were 0.1–0.3 cm³ and were determined by mercury calibration to an accuracy of $\pm 0.1\%$. The volumetric flow-rate of the carrier gas in the course of the measurements was 40 cm³/min and it was changed only during the initial purification and scrubbing of the catalyst samples. The volumetric flow-rate of oxygen and hydrogen was about 20 cm³/min.

Before the actual chemisorptive examination, the sample of catalyst was standardized by passing the carrier gas through it at 600 °K for 1 h and by its reduction at the same temperature with a stream of hydrogen for 1 h. The sample was then scrubbed with carrier gas for 1 h at 600 °K and cooled during the continuous flow of the gas.

It appeared from the initial examination that prolonging both the time of reduction and the time of scrubbing of the sample to 7 h does not affect the results. The surface of palladium prepared in such a manner was considered to be "clean". This was confirmed by the constant sorption ability of the sample with respect to oxygen and hydrogen, independent of the number of oxygen–hydrogen and hydrogen–oxygen titration cycles in the temperature range 300–470 °K (Fig. 1).

The constant sorption ability at a given temperature, independent of the number of titration cycles made on the surface of palladium, proves the regenerative ability of the active surface of palladium after every titration reaction, and also confirms the "cleanness" of the surface after the initial standardization of the catalyst sample.

RESULTS AND DISCUSSION

Fig. 1 gives the results of the titration of the oxygenated surface of palladium by means of hydrogen, $V_{H_2}^O$, and the results of the titration of the hydrogenated surface with oxygen, $V_{O_2}^H$. The results are presented as a function of the number of suc-

cessive titrations for a palladium-silica catalyst containing 0.78% of palladium. It can be seen that the results of the titration carried out at room temperature differ only slightly from those obtained at 373 °K.

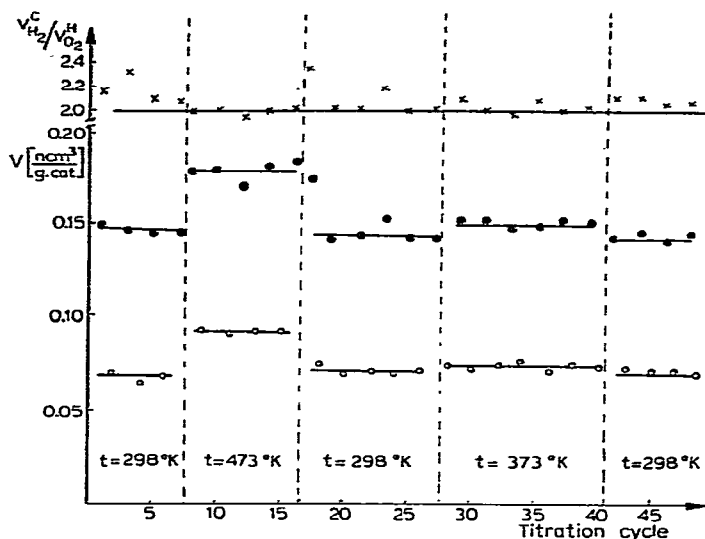
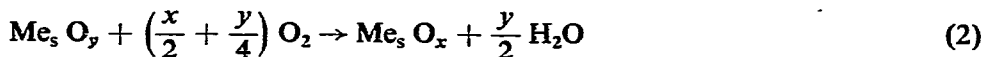
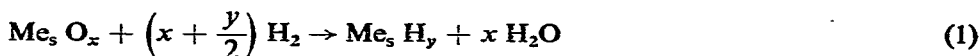


Fig. 1. Dependence of $V_{H_2}^0$ and $V_{O_2}^H$ values on the cycle number at different temperatures for Pd-SiO₂ catalyst (0.72% Pd).

However the values obtained at 573 °K are about 30% greater than those obtained at room temperature. In the upper part of Fig. 1 are also given the values of the stoichiometry of the titration reaction as the ratio $V_{H_2}^0/V_{O_2}^H$, which denotes the ratio of the volume of the hydrogen consumed in the reaction with the oxygenated surface of palladium ($V_{H_2}^0$) to the volume of oxygen necessary in the reverse reaction with hydrogen chemisorbed on the surface of the metal ($V_{O_2}^H$). The value of this ratio is close to 2. The processes of chemisorption of hydrogen and oxygen and the reactions of gas titration that occur on the surface of the metallic phase can be represented by means of two general equations:



where Me_s is a surface atom of the metal and x and y are coefficients determining the stoichiometry of interaction of oxygen and hydrogen, respectively, with surface atoms of the metal. If in eqn. 1 we assume $x = 0$ and in eqn. 2 $y = 0$, then the equations describing the chemisorption of oxygen and hydrogen on the "clean" surface of the metal are obtained.

From eqns. 1 and 2, the quantitative ratio of hydrogen consumed in reaction

1 to oxygen consumed in reaction 2 is $(x + [y/2])/([x/2] + [y/4]) = 2$. It should be noted that the value of this ratio does not depend on particular values of y or x , and it is therefore independent of the stoichiometry of the chemisorptive interaction of oxygen and hydrogen with the atoms of the metal.

The good agreement of the experimentally obtained values of the stoichiometry $H:O = 2$ (Fig. 1) at various temperatures proves that non-chemisorption processes do not occur under the conditions examined, such as reversible hydrogen absorption, the effect of impurities and the hydrogen spillover effect¹⁰. Such reasoning is also correct when the reaction of the metal with oxygen is not limited to the surface atoms only, but also occurs in the interior of the metal. It concerns mainly the titration of oxygenated palladium with hydrogen.

Fig. 2 shows the amounts of hydrogen consumed in the titration of previously chemisorbed oxygen on palladium black *versus* temperature in the range 373–573 °K. The temperature of 373 °K was chosen in view of the significant solubility of hydrogen in palladium at lower temperatures. The measurements were carried out at 50 °K intervals. If at a given temperature the results became stable, the measurements were continued at the next temperature level. The results indicate a considerable influence of exothermic effects in the titration reactions of oxygen and hydrogen at a given temperature on sintering the palladium black (passing from curve 1 to curve 2, Fig. 2). It has been found that above 473 °K it becomes difficult to obtain reproducible oxygen peaks on the register depending on the frequency of injection. The results indicate that starting from 473 °K considerable oxidation of palladium in the bulk metal occurs.

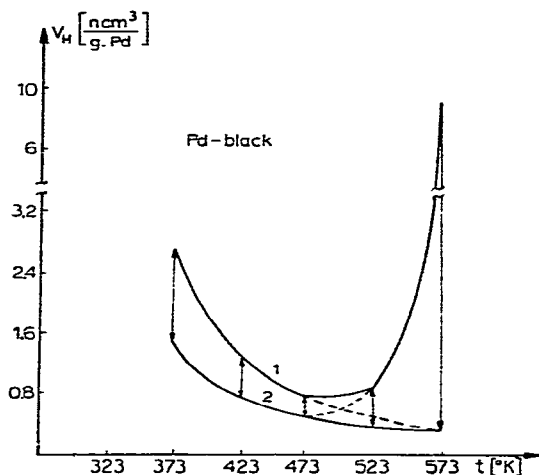
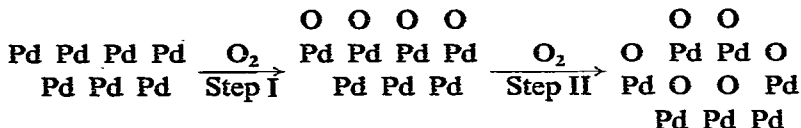


Fig. 2. Amounts of hydrogen consumed with oxygenated surface of palladium black *versus* temperature.

Fig. 3 shows the results of the sorption of oxygen on palladium-silica and palladium-alumina catalysts within the temperature range 300–900 °K. In Fig. 3, one can easily discern three temperature ranges. In the first range, 300–473 °K, sorption of oxygen increases slightly as the temperature is increased; this dependence is linear. The results obtained at 473 °K exceed those obtained at 300 °K by about 30%. In

this range, sorption of oxygen was measured directly and the measurements of chemisorption were carried out on a "clean" surface of palladium. Within it, a considerable increase in the sorption of oxygen occurs as the temperature is increased. This growth can be ascribed to the mutual exchange of places of sorbed oxygen and the surface atoms of metal, *i.e.*, the so-called place-exchange mechanism¹¹. Thus, in general, the adsorption process of oxygen on a "clean" surface of palladium can be represented schematically by



The participation of step II, with deep chemisorption of oxygen as a result of the place-exchange mechanism, which is an activated process, increases as the temperature is increased. It seems possible that step II plays an important role in the second temperature range (473–770 °K). The data given in Fig. 3 relate to the oxidation of samples of catalysts with a stream of oxygen for 1 h; when the samples were oxygenated even for 20 or 40 h they did not undergo further considerable changes. The amount of oxygen absorbed by palladium was determined by titration with pulses of hydrogen after the previous scrubbing of the samples with argon for 1 h at the measurement temperature. It can be assumed that above 470 °K under pulse-dynamic conditions hydrogen does not undergo absorption or it is chemisorbed in negligible amounts on the surface of palladium.

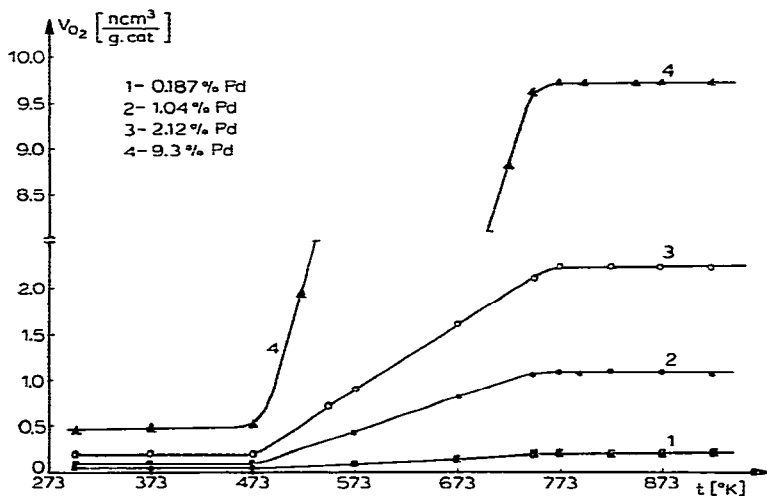


Fig. 3. Sorption of oxygen *versus* temperature for Pd-SiO₂ and Pd-Al₂O₃ catalysts.

The possible chemisorption corrections would be very small in comparison with the results of titration and they would be within the limits of the experimental error, which amounted to about $\pm 2\%$ for an average value.

The third range covers temperatures higher than 770 °K; within this range

the sorption of oxygen does not change as the temperature is increased. The results were determined as in the second temperature range.

In some studies^{6,7} the possibility of forming mobile palladium oxide was stated, but it should be noted that it is valid only with respect to the stoichiometry of oxidation as the temperature increases (473–770 °K). It does not concern the stability of an oxide compound with time, or at temperatures lower than the temperature of oxidation of the catalyst. In this temperature range, the O:Pd stoichiometry of PdO_x increases as the temperature is increased; at about 470 °K $x = 0$ (apart from oxygen chemisorbed on the metal surface), whereas above 770 °K $x = 1$.

In the third temperature range (above 770 °K), sorption of oxygen does not change and $x = 1$. However, above 920 °K palladium oxide decomposes and oxygen is liberated. As was shown by differential thermal analysis, the stability of the O:Pd stoichiometry in palladium oxide (PdO) is preserved up to about 1120 °K. At this temperature, thermal dissociation of the oxide occurs (Fig. 4) into oxygen and the metal. The derivatographic determination was carried out in a stream of argon containing small, uncontrolled amounts of oxygen. The measurements made in a stream of air gave curves identical with those in Fig. 4.

The thermogravimetric (TG) curve illustrating the change of mass as a function of temperature shows an analogous course to the curve of sorption of oxygen

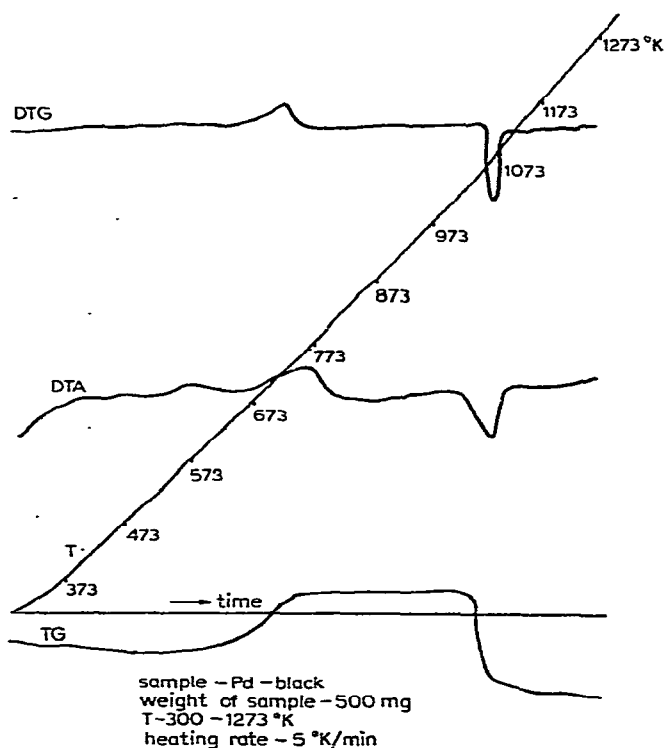


Fig. 4. Thermal analysis of palladium black. TG, weight change of sample; T, temperature curve; DTG, weight derivative of temperature; DTA, temperature changes of sample with respect to standard.

for the same temperature range (300–930 °K). The stability of the sample in the temperature range 770–1120 °K can also be seen from Fig. 4. This stability corresponds to palladium oxide in equilibrium with oxygen. At about 1120 °K a rapid decrease in mass occurs, which is connected with the decomposition of palladium oxide.

In Table I the results of the quantitative determination of palladium in catalysts by two methods (a gravimetric method with the use of dimethylglyoxime, and titration of oxygenated palladium-support catalysts with hydrogen at 790 °K) are presented. The results of the two methods are in good agreement and indicate that complete oxidation of the palladium phase occurs at this temperature.

The results in Table I suggest that the method of titration of the oxygenated palladium catalyst with hydrogen could be applied to the determination of the palladium content of palladium-support catalysts. It is a rapid, convenient method, does not destroy the sample and the determination can be repeated several times.

TABLE I

COMPARISON OF QUANTITATIVE DETERMINATION OF PALLADIUM CONTENT BY A GRAVIMETRIC METHOD AND BY TITRATION OF OXYGENATED PALLADIUM WITH GASEOUS HYDROGEN

Catalyst	Pd (%)		Relative difference $\left[\frac{\text{titration (\%)} - \text{gravimetric (\%)}}{\text{gravimetric (\%)}} \right]$
	Titration method	Gravimetric method	
10% Pd black + 90% Al ₂ O ₃	67	100	-33
Pd-Al ₂ O ₃	9.80	10.0	- 2.0
Pd-Al ₂ O ₃	2.48	2.50	- 0.8
Pd-SiO ₂	2.05	2.12	- 3.3
Pd-SiO ₂	1.79	1.87	- 4.3
Pd-Al ₂ O ₃	1.64	1.72	- 4.6
Pd-SiO ₂	1.00	1.04	- 3.8
Pd-SiO ₂	0.777	0.787	- 1.3

The problem of oxidation of palladium black is slightly different. It has been found that complete oxidation of palladium black to palladium oxide under our conditions is impossible. Palladium black undergoes sintering to a high degree at such high temperatures. The dispersion of palladium in palladium-alumina catalyst amounted to several percent, whereas for the mechanical mixture of palladium black and alumina it was less than 0.01 %. The latter value suggests that palladium black contains a relatively large proportion of massive metal.

The complete bulk oxidation of the palladium phase in palladium-support catalysts suggests the possibility of increasing the dispersion of fresh palladium catalysts (after preliminary reduction), and also the possibility of re-dispersion of the already sintered catalyst as a result of both overheating the catalyst and its participation in a catalytic process.

Fig. 5 shows the effect of oxidation of a palladium-alumina catalyst containing 10% of palladium on the surface of the palladium phase measured by chemisorption of oxygen (V_{O_2}) on a "clean" surface of the metal at room temperature. Oxidation of the catalyst at the given temperature was carried out for about 20 h

in a stream of oxygen with a volume flow-rate of about 10 cm³/min. After oxidation, reduction in a stream of hydrogen was carried out at 570 °K for 2 h, and then the sample was scrubbed with the carrier gas for 1 h and cooled in a stream of carrier gas to room temperature, followed by measurement of oxygen chemisorption.

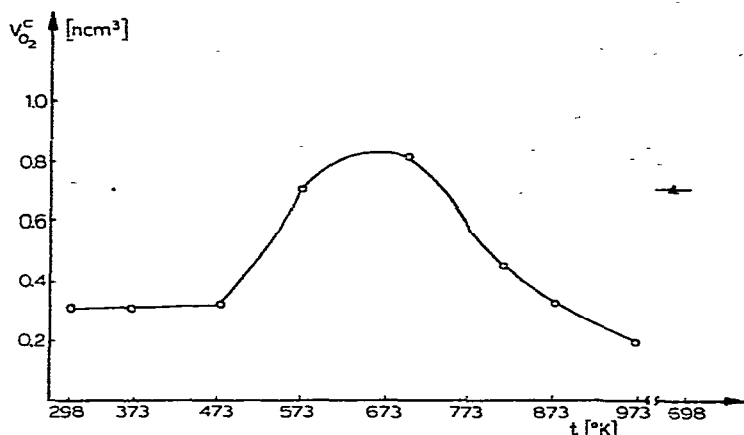


Fig. 5. Effect of oxidation of 10% Pd-Al₂O₃ catalyst.

Fig. 5 indicates that oxidation of a catalyst at temperatures up to 470 °K has virtually no effect on the dispersion of palladium. At temperatures higher than 470 °K a significant increase in the surface area of the metal occurs, with a maximum at about 650 °K. Oxidation at higher temperatures again leads to a decrease in the dispersion of palladium. In spite of the fact that higher temperatures ensure an increase in the degree of oxidation of palladium (Fig. 3), repeated sintering of a catalyst occurs on account either of an increase in temperature or of considerable heat effects connected with the reduction of oxygenated palladium, or both.

In a few instances at 690 °K we managed to obtain results twice as great as those shown in Fig. 5. However, repeated measurements led to a lower result and an average value for a given temperature. It seems possible that palladium structures with large surface areas are formed, but their formation should be considered as exceptional. They are probably unstable structures that deteriorate under the exothermic effects of the titration reaction.

It should be added that the results in Fig. 5 are average values of at least two measurements. The spread of the results usually did not exceed $\pm 5\%$ of the average value for a given temperature. The results obtained show a great influence of an oxidation process with palladium catalysts on the degree of development of the metallic phase. This should be borne in mind when preparing palladium catalysts and when the possibility of re-dispersion of already sintered catalysts is being considered.

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