CHROM. 10,637

INTERACTION OF OXYGEN AND HYDROGEN WITH PLATINUM IN PULSE GAS CHROMATOGRAPHY

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(First received July 11th, 1977; revised manuscript received October 6th, 1977)
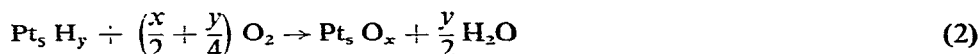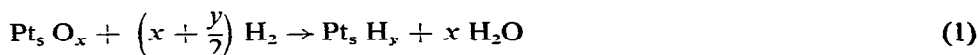
SUMMARY

The interaction of oxygen and hydrogen with the surfaces of platinum black, platinum–silica and platinum–alumina catalysts within the temperature range 196–970 °K was examined by pulse gas chromatography. Chemisorption of oxygen and hydrogen was carried out on a "clean" platinum surface and titrations of the oxidized surface with hydrogen were performed together with those of the reverse reaction, *i.e.*, titration of the reduced surface with oxygen.

We were able to define the extent of slow, reversible hydrogen sorption within a wide temperature range, desorption of oxygen from the platinum surface and the formation of an oxide multilayer at high temperatures. The results indicate that the stoichiometries of the surface interactions between platinum and oxygen and between platinum and irreversibly chemisorbed hydrogen are the same and approximate to unity: $O/Pt_s \approx H/Pt_s \approx 1$. The temperature range 300–570 °K is suitable for determining platinum dispersions by means of oxygen and hydrogen chemisorption.

INTRODUCTION

Many papers have been devoted to investigations of the interaction of oxygen with platinum[1–18], but in spite of considerable achievements many problems have not yet been solved. The experimental conditions (temperature, pressure, type and purity of samples) used in the adsorption processes described in the above papers were often different and thus the results were not comparable. This is particularly true of the stoichiometry of the interactions of oxygen and hydrogen with platinum surface atoms (Pt_s).

In order to define the character of the interactions, we also used reactions of gas titration between hydrogen from the gaseous phase and oxygen previously chemisorbed on the platinum surface (reaction 1). The reverse reaction, *i.e.*, between oxygen from the gaseous phase and hydrogen adsorbed on the metal surface (reaction 2), can also be of great help.

$$Pt_s\, O_x + \left(x + \frac{y}{2}\right) H_2 \rightarrow Pt_s\, H_y + x\, H_2O \tag{1}$$

$$Pt_s\, H_y + \left(\frac{x}{2} + \frac{y}{4}\right) O_2 \rightarrow Pt_s\, O_x + \frac{y}{2} H_2O \tag{2}$$

where Pt_s is a platinum surface atom and x and y represent the stoichiometry of interactions of platinum surface atoms with oxygen and hydrogen.

If we assume that in the first equation $x = 0$ and in the second $y = 0$, then the above equations describe simple processes of chemisorption of hydrogen and oxygen, respectively, on a "clean" metal surface. From these equations, it follows that the ratio of the amount of hydrogen used in the first reaction to the amount of oxygen used in the second (eqn. 3) is 2. It does not depend on the stoichiometry of the interactions of oxygen (x) and hydrogen (y) with the platinum surface.

$$\frac{x + \dfrac{y}{2}}{\dfrac{x}{2} + \dfrac{y}{4}} = 2 \tag{3}$$

The value of this ratio can be used for testing whether the reactions of oxygen and hydrogen with metals are only simple and fast chemisorption processes.

If the experimental values of this ratio differ from 2, it may indicate the occurrence of processes accompanying the fast chemisorption. Such non-chemisorption processes may include the following:

(1) physical adsorption processes (on the metal or carrier);

(2) absorption processes;

(3) processes of bulk formation of compounds;

(4) processes of migration of the previously chemisorbed adsorbate atoms towards a support (spill-over processes).

There is a need for systematic investigations to give a better knowledge of surface interactions of platinum with oxygen and hydrogen over a wide temperature range by means of pulse gas chromatography, and such studies are reported in this paper.

EXPERIMENTAL

The investigations were conducted by means of pulse chromatographic methods. The apparatus used and the method of measurement have been described earlier[22,23]. The choice of suitable measurement conditions (mainly the purity of the carrier gas and its flow-rate, temperature of measurement, volume of the pulse introduced and frequency of injection) have previously been considered, and also the amount of catalyst with respect to the content of metal and the degree of dispersion[15,19–24]. Argon appeared to be the most suitable gas for our investigations. Its chemisorptive passivity, low thermal conductivity and high degree of purity give suitable conditions that lead to reproducible adsorption results on metal surfaces.

The size of the oxygen and hydrogen pulses injected was usually $ca.$ 0.1 cm³ (sometimes 0.3 cm³) and these were graduated precisely with mercury beforehand. The amounts of catalyst used in adsorption measurements (grains of dimensions 0.2–0.5 mm) depended on the content of metal and usually ranged from 1 to 5 g.

No oxygen and hydrogen adsorptive effects on alumina and silica were observed over the whole range of temperatures investigated (196–970 °K).

In the above respect chromatographic methods are superior to static methods as the latter require some corrections for physical adsorption on the carriers.

The catalysts used, *i.e.* platinum–silica and platinum–alumina, were obtained by adsorption or impregnation methods from solutions of suitable salts. They were then dried and calcined in oxygen or air and finally reduced with hydrogen.

In our investigations we used platinum black (Johnson Matthey Chemicals, London, Great Britain) with a specific surface area of 2.5 m²/g determined by the B.E.T. method, *i.e.*, low-temperature adsorption of krypton.

Before being used in adsorption investigations, the catalysts were processed as follows in order to obtain "clean" metallic surfaces. The catalyst, after being placed in the adsorption reactor, was "purged" with a carrier gas, usually for 1 h at 773 °K, in order to remove adsorbed moisture from the sample and other adsorbed impurities from the metal surface and the support. The catalyst was then exposed to hydrogen at the same temperature for 2 h. After the reduction, carrier gas was again passed through the layer of catalyst for 1 h, then the sample was cooled in a stream of the carrier gas to the temperature at which the adsorption measurements were to be performed.

RESULTS AND DISCUSSION

A typical chromatogram of oxygen adsorption on a sample of a catalyst is presented in Fig. 1. The oxygen peaks are very sharp and symmetrical.

The peak resulting from injection of hydrogen is slightly different (Fig. 2). If the shapes of the hydrogen peaks for a silica carrier are compared with those for a platinum–silica catalyst, a clearly extended sloping line can be seen for the latter.

The peak shown in Fig. 2b is the first hydrogen peak recorded, so its shape characterizes the interaction between hydrogen and the platinum surface previously reduced with irreversibly adsorbed hydrogen.
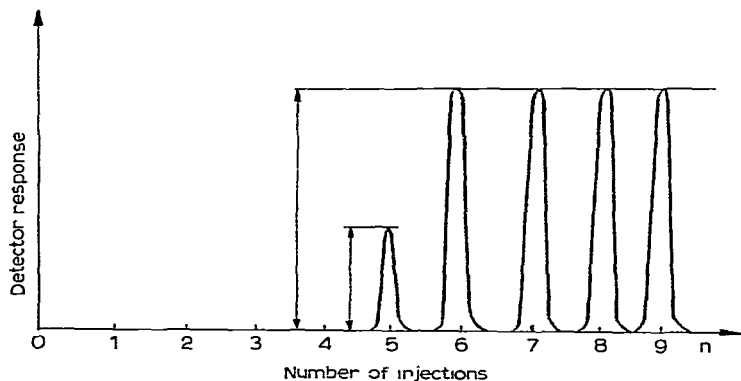

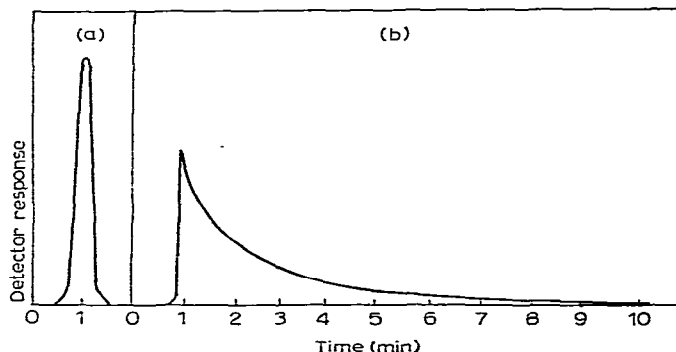Fig. 1. Typical chromatogram of oxygen chemisorption on a platinum surface.

Fig. 2. Detector response to hydrogen injections: (a) after passing through a silica layer; (b) after passing through an equivalent layer of platinum–silica catalyst (1.63% Pt).

As far as the time of reaction is concerned, hydrogen undergoes a relatively long reaction with the platinum surface, which indicates the existence of a weak reversible form of hydrogen adsorption on the surface of the metal.

We defined the conditions that must be satisfied in order to prepare "clean" surfaces of metallic platinum catalysts. A "clean" surface means a surface on which adsorptive properties are permanent and there are no surface impurities.

Taking into account the efficiency and extent of deoxygenation of a carrier gas obtained by the use of manganese(II) oxide[23,24], it seems justifiable to assume that oxygen was absent in the measurement conditions used in our work. This is illustrated by Fig. 3, where the stability of the oxygen adsorption results proves indirectly the lack of oxygen in the carrier gas.
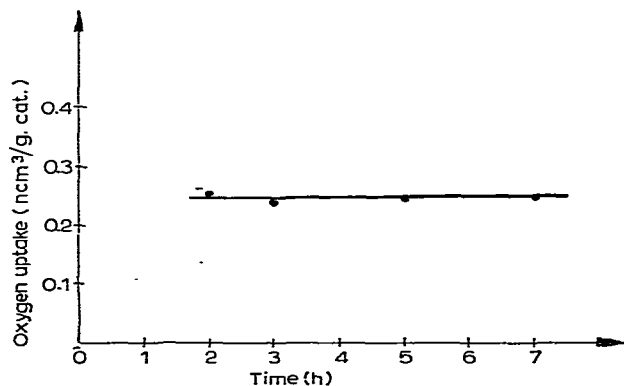

Fig. 3. Influence of the time of "rinsing" with carrier gas on reproducibility of oxygen sorption results. ncm^3 = cm^3 at standard temperature and pressure conditions.

The influence of the flow-rate of the carrier gas on the adsorption of oxygen and hydrogen on the platinum surface at 196 and 300 °K is illustrated in Fig. 4.
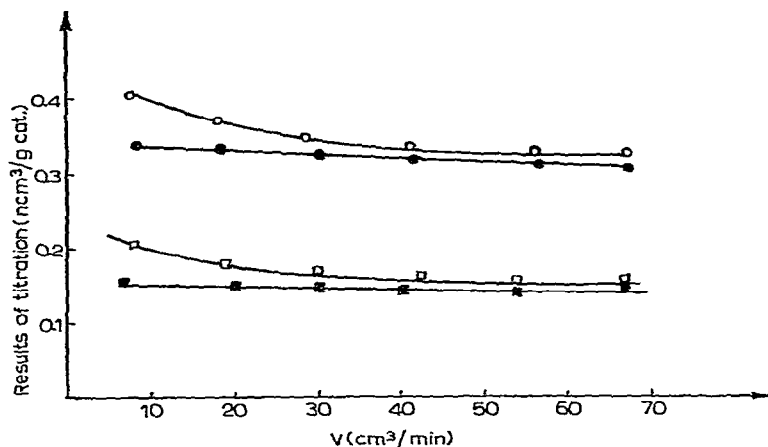
Fig. 4. Results of oxygen–hydrogen and hydrogen–oxygen titrations depending on the flow-rate of argon for platinum–silica catalyst (1.4% Pt). Hydrogen titration at (○) 196 °K and (●) 300 °K; oxygen titration at (□) 196 °K and (■) 300 °K.

Fig. 4 shows that an increase in the flow-rate of the carrier gas is accompanied by a considerable decrease in the amount of hydrogen used in titration of the oxidized surface, especially at 196 °K. This fact may be attributed to the occurrence of weak and irreversible hydrogen adsorption during fast chemisorption[1-4], particularly at 196 °K. The sum of the reversibly and irreversibly adsorbed hydrogen is approximately the same as the amount of the gas adsorbed at ambient temperature. An increase in the flow-rate of the carrier gas over 40 cm³/min does not have a great influence on the results, indicating that weak reversible hydrogen adsorption occurs to an insignificant extent. The results of hydrogen titration of previously oxidized platinum black as a function of temperature are presented in Fig. 5. At each temperature the oxidized
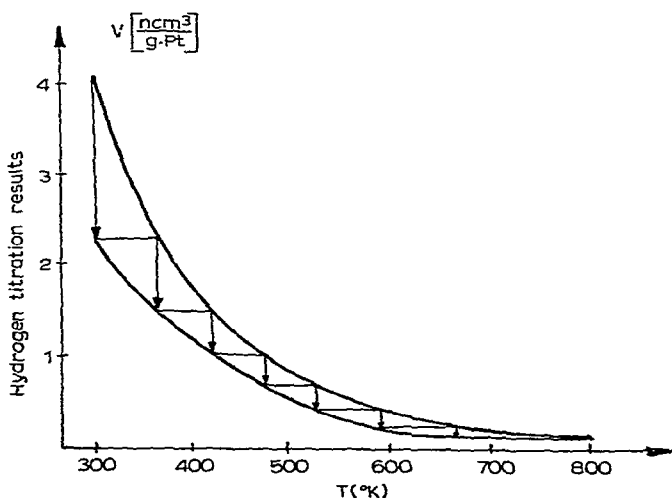

Fig. 5. Results of titration of previously oxidized platinum black with hydrogen depending on temperature.

platinum black was titrated several times with hydrogen until a constant result was established. This procedure was necessary because during the measurements a decrease in $V_H{}^o$ (volume of hydrogen consumed in reaction 1) and $V_O{}^r$ (volume of oxygen consumed in reaction 2) (represented in Fig. 5 by perpendicular arrows) took place owing to sintering of the platinum black, mainly because of exothermic effects that occurred during the titration process.

The sintering of platinum black is dependent only to a very small extent on the temperature used in the titration reactions (shown in Fig. 5 by horizontal arrows).

Exothermic effects in the titration reaction resulted in a considerable local increase in the temperature of a sample above the measurement temperature. After the establishment of $V_H{}^o$ and $V_O{}^r$ values at a particular temperature, the temperature of the measurements was increased by *ca.* 50 °K (horizontal arrows in Fig. 5).

The specific surface area of platinum black after a complete measurement cycle was reduced considerably, from 2.5 to below 0.1 m²/g.

In order to avoid the effects due to sintering of platinum black at higher temperatures, platinum supported on alumina and silica (Table II) was used. A typical example of the titration results with platinum supported on a carrier is shown in Fig. 6.
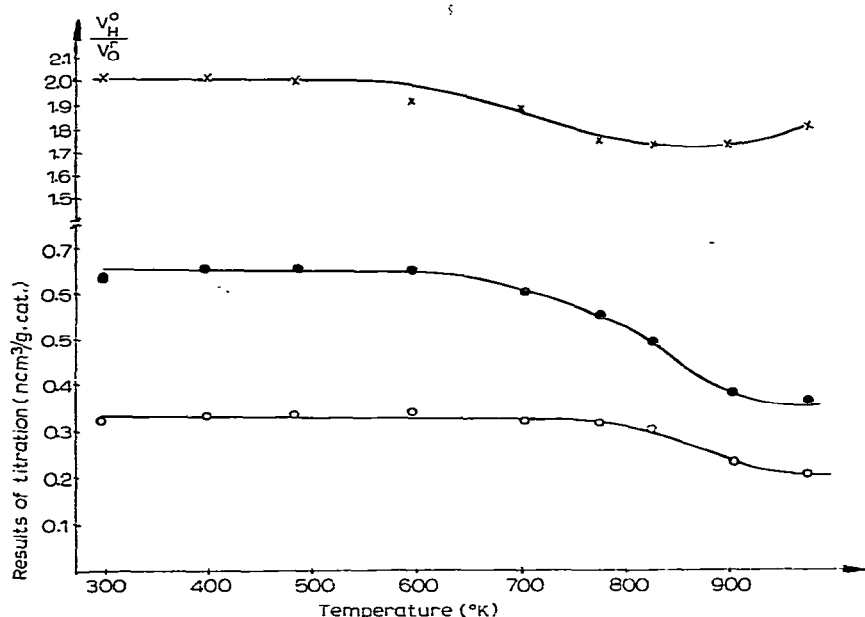

Fig. 6. Results of titration reactions depending on temperature using a platinum–silica catalyst (1.63% Pt). ●, Hydrogen titration ($V_H{}^o$); ○, oxygen titration ($V_O{}^r$); ×, ratio $V_H{}^o/V_O{}^r$.

From Fig. 6, it follows that within the temperature range 300–570 °K the value of $V_H{}^o/V_O{}^r$ is *ca.* 2. At temperatures higher than 570 °K, $V_H{}^o$ decreases and $V_H{}^o/V_O{}^r$ also decreases to values below 2; up to 770 °K, $V_O{}^r$ is virtually constant. Fig. 6 indicates that within the range 300–570 °K there are no essential changes in the reactions of oxygen and hydrogen with the platinum surface and platinum dispersion can be determined by the reaction of gaseous titration.

As has already been mentioned, the value of $V_H{}^o/V_O{}^r$ should be 2 if pure processes of oxygen and hydrogen chemisorption on the platinum surface occur in the measurement system. If, however, the chemisorption processes are accompanied by some additional, non-chemisorption processes, a value of the $V_H{}^o/V_O{}^r$ ratio different from 2 may indicate the occurrence of processes that accompany the fast chemisorption of oxygen and hydrogen. The decrease in this ratio above 570 °K indicates that partial oxygen desorption may be the additional process. Thus, part of the oxygen adsorbed on the platinum surface may be desorbed into a stream of carrier gas in such a way that hydrogen can subsequently be used for the titration of the remaining strongly adsorbed oxygen. This process results in an apparent decrease in $V_H{}^o/V_O{}^r$. This suggestion is confirmed by the experimental results in Table I. A sample of a catalyst was oxidized at ambient temperature and then heated to *ca.* 900 °K. After cooling to ambient temperature, additional oxygen adsorption was carried out and then the sample was re-heated to 900 °K. This cycle was repeated several times. Finally hydrogen titration of the whole of the adsorbed oxygen was performed at 900 °K.

TABLE I

RESULTS OF MEASUREMENTS OF OXYGEN DESORPTION FROM A PLATINUM-SILICA CATALYST (1.63% Pt)

No. of cycle	Volume of adsorbed oxygen at ambient temperature, $V_O^{300\ °K}$ (ncm³ per gram of catalyst)	Volume of hydrogen used for titration of oxygen, $V_H^{900\ °K}$ (ncm³ per gram of catalyst)	$\frac{1}{2} V_H^{900\ °K}$ (ncm³ per gram of catalyst)	Volume of desorbed oxygen, $\Sigma V_O^{300\ °K} - \frac{1}{2} V_H^{900\ °K}$ (ncm³ per gram of catalyst)
0	0.953	3.22	1.61	1.11
1	0.414			
2	0.240			
3	0.375			
4	0.410			
5	0.328			
$\Sigma V_O^{300\ °K}$	2.720			

The results indicate that at higher temperatures oxygen is not only sorbed into the interior of platinum surface layers (about 10 monolayers at 920 °K), but is also desorbed from the platinum surface into the gaseous phase.

At ambient temperature, however, it can be assumed that oxygen, under the conditions of the pulse chromatographic method, undergoes only fast irreversible adsorption. The platinum surface, having once been oxidized at 300 °K, did not sorb additional portions of oxygen even after prolonged rinsing of the sample with argon. The results of these measurements and of analogous measurements performed on palladium[19] indicate that oxygen–platinum reactions are very different to oxygen–palladium reactions. With palladium at high temperatures, complete oxidation of the metal occurs, together with the formation of bulk oxide. With platinum, however, the reactions with oxygen preserve their superficial character, although oxygen chemisorption is accompanied by incorporation of oxygen into the metallic phase.

The results of the titration reactions are in fact overall values for oxygen and hydrogen chemisorption on platinum (eqns. 1 and 2) and therefore they do not directly represent the sorptive properties of platinum in relation to oxygen or hydrogen. Thus mutual compensation of the quantitative changes in oxygen and hydrogen chemisorption may occur, with the possibility of neglecting the changes in the values of V_H° and V_O^r. For this reason, on the same catalyst sample we performed measurements of hydrogen chemisorption, V_H^C (V_H^C = volume of hydrogen chemisorbed on the "clean" catalyst surface), and oxygen chemisorption, V_O^C (V_O^C = volume of oxygen chemisorbed on the "clean" catalyst surface), on a clean platinum surface within the range 300–670 °K. The results of the measurements and those of V_H° and V_O^r titrations are presented in Fig. 7.
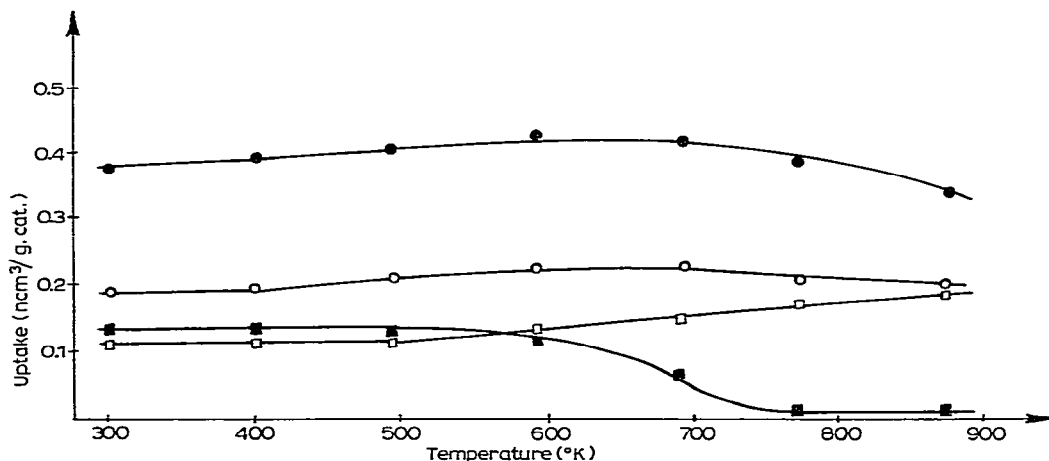

Fig. 7. Results of oxygen and hydrogen chemisorption from titrations of oxidized samples with hydrogen and titrations of reduced samples with oxygen, depending on temperature. □, Oxygen chemisorption (V_O^C); ■, hydrogen chemisorption (V_H^C); ○, oxygen titration (V_O^r); ●, hydrogen titration (V_H°).

The results in Fig. 7 illustrate the usefulness of the temperature range 300–500 °K for determining platinum dispersion. It refers generally to all four adsorptive methods: oxygen chemisorption on the clean surface (V_O^C), hydrogen chemisorption on the clean surface (V_H^C), titration of the reduced surface with oxygen (V_O^r) and the reverse reaction titration of the oxidized surface with hydrogen (V_H°). Table II presents the results of determinations of platinum dispersions in platinum–silica and platinum–alumina catalysts. The results were obtained by the above four methods at ambient temperature.

For the sake of comparison, results of hydrogen chemisorption obtained under static conditions at 520 °K are given for platinum–alumina catalysts. Table II also contains the differences between the results of oxygen and hydrogen chemisorption.

The results of hydrogen chemisorption are generally higher than those of oxygen chemisorption, the maximal differences being not more than 30%. This difference is connected with the presence of slow and reversible hydrogen adsorption accompanying fast and irreversible hydrogen chemisorption. The contribution of the slow chemisorption at ambient temperature in pulsed gas chromatography (under our

TABLE II

RESULTS OF OXYGEN AND HYDROGEN ADSORPTION AND OF TITRATIONS IN THE OXYGEN–HYDROGEN SYSTEM OBTAINED FOR PLATINUM–SILICA AND PLATINUM–ALUMINA CATALYSTS

Catalyst	Pt (%)	H/Pt	O/Pt	Pt_s/Pt^*	Pt_s/Pt^{**}	H/Pt^{***}	$\dfrac{H/Pt - O/Pt}{H/Pt}$ (%)
Pt-SiO₂	2.78	0.087	0.088	0.097	0.099		−1
	1.63	0.19	0.17	0.19	0.19		+11
	1.63 §	0.12	0.10	0.11	0.11		+7
	1.20	0.27	0.22	0.24	0.23		+19
Pt-Al₂O₃	1.39	0.12	0.12	0.14	0.13	0.10	0
	0.88	0.15	0.11	0.12	0.12	0.17	+27
	0.62	0.31	0.25	0.24	0.24	0.20	+19
	0.52	0.36	0.26	0.37	0.34	0.25	+28
	0.36	0.38	0.29	0.35	0.34	0.35	+25

* Results of titration of the oxidized surface with hydrogen.

** Results of titration of the reduced surface with oxygen.

*** Results of hydrogen chemisorption under static conditions at 520 °K (all other results were obtained at ambient temperature).

§ Catalyst was "rinsed" with argon for 16 h at 920 °K.

conditions) is *ca.* 20%. Taking into account reversible hydrogen sorption, we could achieve a reasonable agreement of the results in Table II.

It therefore seems that the stoichiometries of the surface reactions of platinum with oxygen and irreversibly chemisorbed hydrogen are almost the same at ambient temperature and approximate to unity: $O/Pt_s \approx H/Pt_s \approx 1$. The results of platinum dispersion obtained from the titration reactions (oxygen–chemisorbed hydrogen and hydrogen–chemisorbed oxygen) given in Table II agree with the results of oxygen chemisorption. They are also in agreement with hydrogen irreversibly chemisorbed on a "clean" platinum surface.

The results of platinum dispersion on the basis of titration reactions were obtained by assuming the existence of the simple stoichiometry $H/Pt_s = O/Pt_s = 1$. Thus, taking into account their agreement with the results of hydrogen and oxygen chemisorption on the "clean" platinum surface, the conclusion can be drawn that the H/Pt_s and O/Pt_s stoichiometries are not only nearly equal but they approximate to unity. The data are in agreement with the stoichiometry proposed by Vannice et al.[8]. However, it should be stressed that the experimentaly estimated dependence of $H/Pt_s \approx O/Pt_s \approx 1$ refers to irreversible contributions of hydrogen and oxygen. Moreover, it can be assumed that under the conditions of pulse chromatography oxygen undergoes only fast, irreversible adsorption at ambient temperature.

Therefore, it seems that oxygen should be preferable to hydrogen as an adsorbate for determining platinum dispersion. The objection to oxygen as an adsorbate for determining platinum dispersion, with the O/Pt_s stoichiometry depending on the degree of platinum dispersion, seemed not to be confirmed by experiments for dispersions lower than 0.5.

The comparison of the results for hydrogen chemisorption obtained under static conditions at 520 °K with the other results obtained by pulse chromatography

indicates a satisfactory agreement as far as the differences in temperatures and methods of measurement are concerned.

For determining the surface area of platinum, titration reactions (eqns. 1 and 2) are very useful. They are suitable for rapid test determinations of the surface area of platinum in catalysts of the platinum–support type.

In spite of the considerable usefulness of titration reactions for the determination of platinum dispersion, their application gives rise to some problems. These difficulties result not only from doubts (not entirely explained) concerning simple oxygen and hydrogen stoichiometries, but also from some new problems caused by the application of the very reaction gaseous titration. An example of the latter is the dependence of the results of the titration reactions on the number of titration cycles on a platinum–silica catalyst with a platinum content of 1.63%.

The investigations for which the results are presented in Fig. 8 were conducted at ambient temperature. Each series of titration cycles was preceded by "cleaning" of the sample surface. The vertical broken lines mark the stages at which a "clean" surface of the platinum was used in the catalyst. From Fig. 8, it follows that after each cleaning stage, V_H^o and V_O^r increase as the number of succeeding measurement cycles increases. The increase may be observed in several initial measurement cycles, then V_H^o and V_O^r become constant. The increase is accompanied by a decrease in V_H^o/V_O^r until a value of 2 is reached.

At present, it is difficult to explain the causes of the increases in the curves in Fig. 8. It may be connected with the influence of water formed during the titration process[25], but it is likely that such an explanation is not the only one. It seems even
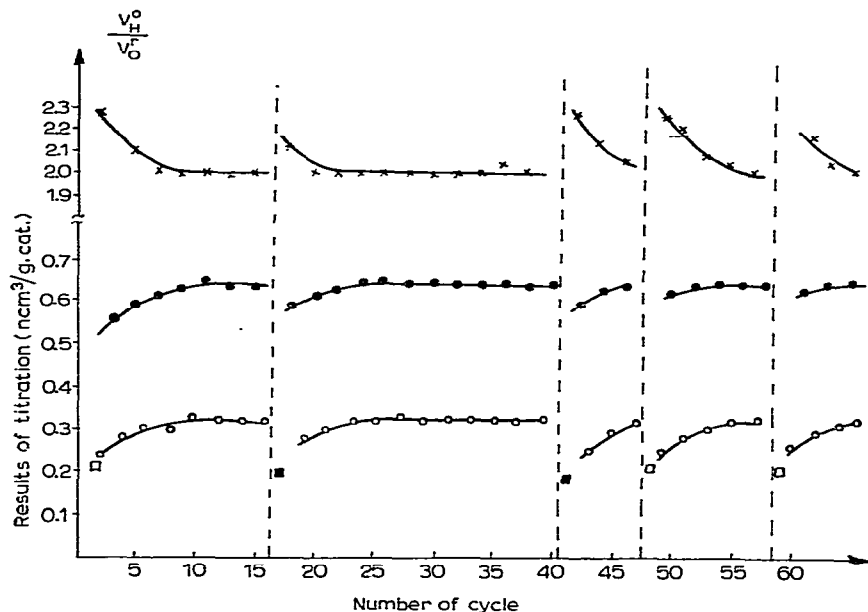

Fig. 8. Results of titration depending on the number of measurement cycles for a platinum–silica catalyst (1.63% Pt). □, Oxygen chemisorption (V_O^c); ■, hydrogen chemisorption (V_H^c); ○, oxygen titration (V_O^r); ●, hydrogen titration (V_H^o); ×, ratio V_H^o/V_O^r.

more problematical when water from outside is introduced into the system; this results in considerable decreases in $V_H{}^o$ and $V_O{}^r$.

Other work[26,27] suggests that the increase in hydrogen sorption as a consequence of the reduction of the oxidized platinum surface is connected with an increase in the surface area, resulting from changes in the orientation of platinum surface atoms in relation to oxygen and hydrogen. It is likely that the increase in $V_H{}^o$ and $V_O{}^r$ is due to impurities in the surface layers of platinum or the support, which may diffuse to the surface during high-temperature treatment (or cooling) of the catalyst. They are then removed during succeeding titration cycles and the whole process ends in the reoccurrence of the sorptive properties of the platinum surface. The situation is illustrated by rectilinear segments of the curves presented in Fig. 8.

The above considerations are only suggestions, and the problem of the increase in $V_H{}^o$ and $V_O{}^r$ values with an increase in the number of titration cycles requires further investigation.

REFERENCES

1 J. R. Anderson, *Chemisorption and Reactions on Metallic Films*, Vol. 1, Academic Press, London, New York, 1971.
2 D. O. Hayward and B. M. W. Trapnell, *Chemisorption*, Butterworths, London, 1964.
3 J. R. Anderson, *Structure of Metallic Catalysts*, Academic Press, London, New York, San Francisco, 1975.
4 V. Ponec, Z. Knor and S. Cerny, *Adsorption on Solids*, Butterworths, London, 1974.
5 G. R. Wilson and W. K. Hall, *J. Catal.*, 17 (1970) 190.
6 G. R. Wilson and W. K. Hall, *J. Catal.*, 24 (1972) 306.
7 C. R. Adams, H. A. Benesi, R. M. Curtis and R. S. Meisenheimer, *J. Catal.*, 1 (1962) 336.
8 M. A. Vannice, J. E. Benson and M. Boudart, *J. Catal.*, 16 (1970) 348.
9 H. L. Gruber, *Anal. Chem.*, 34 (1962) 1828.
10 P. A. Sermon and G. C. Bond, *Catal. Rev.*, 8 (1973) 211.
11 J. E. Benson and M. Boudart, *J. Catal.*, 4 (1965) 704.
12 D. E. Mears and R. C. Hansford, *J. Catal.*, 9 (1967) 125.
13 J. D. Clewley, J. F. Lynch and T. B. Flanagan, *J. Catal.*, 36 (1975) 291.
14 J. Freel, *J. Catal.*, 25 (1972) 139.
15 J. Prasad and P. G. Menon, *J. Catal.*, 44 (1976) 314.
16 W. S. Boronin, O. M. Połtorak, N. N. Smirnowa and A. Lewicki, *Wiestnik Moskowskowo Uniwersyteta*, No. 1, 1975.
17 W. S. Boronin, W. S. Nikulina and O. M. Poltorak, *Zh. Fiz. Khim.*, 46 (1972) 463.
18 H. Kubicka, *J. Catal.*, 12 (1968) 223.
19 T. Paryjczak, W. Jóźwiak and J. Góralski, *J. Chromatogr.*, in press.
20 A. Hausen and H. L. Gruber, *J. Catal.*, 20 (1971) 97.
21 T. Paryjczak, *Chromatografia Gazowa w Badaniach Adsorpcji i Katalizy*, PWN, Warsaw, 1975.
22 T. Paryjczak, W. Jóźwiak and J. Góralski, *J. Chromatogr.*, 120 (1976) 291.
23 T. Paryjczak and K. Jóźwiak, *J. Chromatogr.*, 111 (1975) 443.
24 C. R. Mellwrick and C. S. G. Phillips, *J. Phys. E*, 6 (1973) 208.
25 E. Kikuchi, P. C. Flynn and S. E. Wanke, *J. Catal.*, 34 (1974) 132.
26 I. G. Aston, E. S. I. Tomezsko and R. A. Fisher, *J. Amer. Chem. Soc.*, 86 (1964) 2097.
27 D. J. Darensbourg and R. P. Eischens, *Proceedings of 5th International Congress on Catalysis*, Vol. 1, North-Holland, Amsterdam, 1972, pp. 21–371.