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INTERACTIONS BETWEEN HYDROGEN, OXYGEN AND SUPPORTED IRIIDIUM STUDIED BY PULSE GAS CHROMATOGRAPHY

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SUMMARY

The interactions between oxygen, hydrogen and iridium supported on alumina, and titration reactions on the catalyst surface, have been examined by pulse gas chromatography within the temperature range 193–973° K.

There are two temperature ranges for the different interactions between oxygen and iridium: 193–623° K, within which surface chemisorption dominates; and 623° K where there is considerable oxidation of the bulk catalyst. Two temperature ranges have also been distinguished for the interactions between iridium and hydrogen: 193–243° K, with increasing hydrogen adsorption; and above 243° K, with gradually decreasing hydrogen adsorption. Titration reactions of the oxygen–hydrogen system on the surface of iridium–alumina have been used to determine the iridium dispersion.

INTRODUCTION

Metals in Group VIII of the Periodic Table are, as a rule, good catalysts of many chemical reactions. In particular, platinum has been thoroughly investigated^{1–3}. Since comparatively less attention has been devoted to iridium, the aim of the present paper is to help to fill this gap.

Most investigations of adsorption on supported iridium have been carried out within relatively narrow temperature ranges, mainly by means of static methods^{4,5}. We have investigated the adsorptive interactions between oxygen, hydrogen and supported iridium within quite a wide temperature range, 193–973° K, using a dynamic method. The possibility of applying titration in the oxygen–hydrogen system in order to determine the extent of iridium dispersion has also been studied.

EXPERIMENTAL

Preparation of the catalysts

Iridium trichloride (99% purity) was obtained from Koch-Light (Colnbrook, Great Britain), and alumina from Carlo Erba (Milan, Italy). The catalysts were obtained by the impregnation method^{6,7}. Iridium trichloride was dissolved in redistilled water and after a suitable amount of the alumina support had been added, the water

was evaporated *in vacuo* at ambient temperature. The catalyst was then dried at 378° K for *ca.* 2 h. Before use, the catalyst was reduced in a stream of hydrogen. The temperature of the process was gradually increased to 773° K, and the samples were kept at this temperature for several hours. The total time of reduction was *ca.* 10 h. After completion of the reduction, the carrier gas was passed through the catalyst for *ca.* 1 h at 773° K.

Methods

The apparatus used for the chromatographic measurements, the methods of obtaining hydrogen and oxygen and the gas purification were described previously^{8,9}. The flow-rate of the carrier gas was 50 cm³/min, the results of the measurements being only slightly affected by flow-rate (Fig. 1). The volumes of the adsorbate pulses introduced to the carrier gas were 0.4–2.0 cm³.

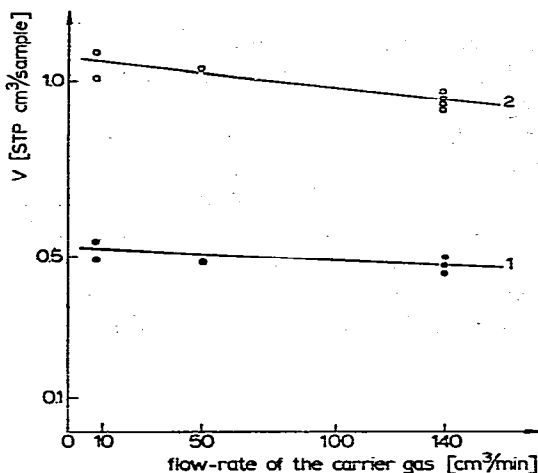


Fig. 1. Dependence of titration results on the carrier gas flow-rate for oxygen (1) and hydrogen (2).

Within the temperature range 199–973° K, no adsorption effects of oxygen and hydrogen on the support surface were observed.

RESULTS AND DISCUSSION

Since adsorption results are strongly dependent on the conditions of catalyst pretreatment, it was necessary to concentrate attention on obtaining a "clean" surface of iridium supported on Al₂O₃. The temperature of the reduction process, 773° K, seems to result in a complete removal of surface impurities and virtually excludes hydrogen adsorption. In order to confirm the absence of hydrogen adsorption, we investigated the influence of the time of flushing with a carrier gas at 773° K (after reduction at the same temperature) on the results of hydrogen adsorption at ambient temperature. The results are presented in Fig. 2. It can be seen that flushing for 15 min is sufficient for practically complete removal of hydrogen from the metal surface. A similar conclusion can be made from the experimental data presented in Fig. 3.

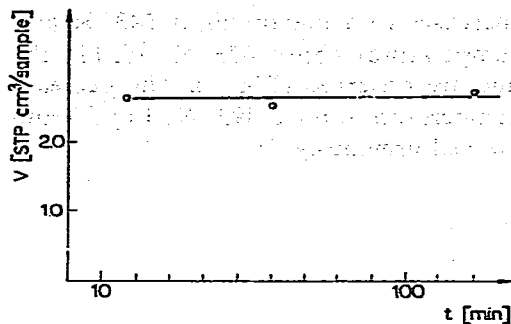


Fig. 2. Dependence of hydrogen adsorption on a "clean" surface on the time of flushing with the carrier gas at 773 °K.

Hydrogen adsorption at 773° K constitutes several percent of the chemisorption at ambient temperature, and exhibits the characteristics of a reversible process. In order to obtain a "clean" surface the following procedure was used. Reduction with hydrogen (continuous or pulsed) at 773° K, flushing with a carrier gas for at least 15 min at the same temperature and finally cooling in a stream of argon to the measurement temperature.

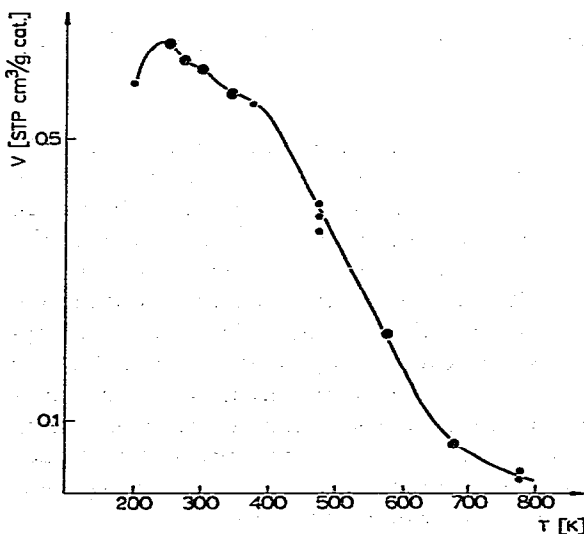


Fig. 3. Hydrogen adsorption on a "clean" surface for a 3% iridium catalyst at different temperatures.

Hydrogen adsorption

Measurements of hydrogen adsorption on the "clean" surface of iridium were carried out at the temperatures from 193 to 773° K and occasionally up to 973° K. The results are presented in Figs. 3 and 4. Near the maximum of hydrogen sorption (close to ambient temperature) Fig. 3 contains more measurement points, since this region is that within which other authors^{4,6,10} assume the existence of a monolayer.

Hydrogen chemisorption starts at 193° K, increases to a maximum at 243° K and then decreases to values close to zero for temperatures above 673° K. Within the temperature range 243–398° K diffuse maxima are observed (Fig. 3). The decrease in hydrogen chemisorption with increasing temperature (above 393° K, Figs. 3 and 4) for the metals of Group VIII has been observed previously^{3,11}.

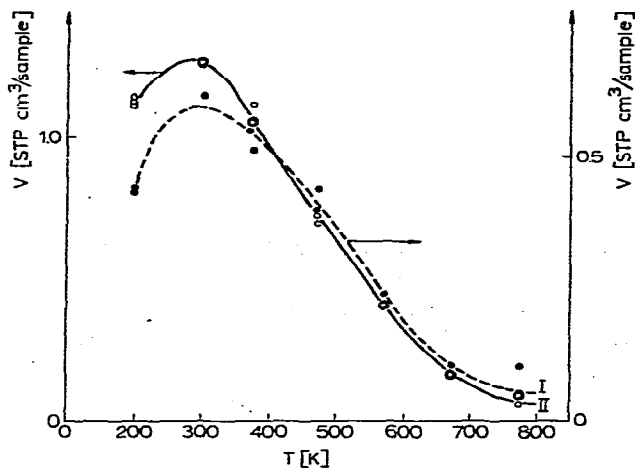


Fig. 4. Hydrogen adsorption as a function of temperature on a 1% iridium catalyst (I) and on a 5% iridium catalyst (II).

Comparison of our experimental data within the temperature range 193–303° K with the thermodesorption results of Escard *et al.*¹² allows assignment of the maximum points of hydrogen chemisorption to three different forms of hydrogen adsorption on iridium. Escard *et al.*¹² attributed the desorption maximum at the lowest temperature (223° K, type α) to molecular adsorption, whereas the two remaining peaks (β_1 at 323° K and β_2 at 393° K) were assigned to weak types of atomic hydrogen adsorption. Sokolski *et al.*¹³ discovered the presence of two forms of hydrogen bonding on an iridium surface for Ir-Al₂O₃ catalysts at 353 and 453° K; however, their measurements were initiated at ambient temperature. This fact seems to account for the lack of a peak originating from the weak (α) hydrogen adsorption. Although our results seem to confirm the existence of the three forms of hydrogen adsorption within the investigated temperature range, the pulse chromatographic method is not the most suitable for the study of weak adsorptions.

Within the range 193–243° K the hydrogen sorption increases with increasing temperature (Fig. 3). This increase could result from the influence of some kinetic factors which inhibit the chemisorption process at decreasing temperature. An experiment was carried out in which, after hydrogen chemisorption at ambient temperature, the temperature was reduced to 193° K and the chemisorptive ability of the sample was again examined. The results are presented in Fig. 5. Despite the lower hydrogen adsorption at 193° K (Fig. 5), the sample revealed considerable sorption properties. It was also found that while heating to ambient temperature a sample that had previously been reduced (point B in Fig. 5) at 193° K, a slight thermodesorption

occurred, which would not have been expected from the results in Fig. 3. Much larger thermodesorptive effects were obtained after repeated reduction at 193° K (point A in Fig. 5). Point C was attained in the same way as point A, by cooling a sample which had previously been reduced at 373° K to ambient temperature. It follows from Fig. 5 that points A and C lie high above the curve of hydrogen chemisorption for a "clean" iridium surface. This behaviour of the iridium-hydrogen system can be explained in terms of the non-equilibrium character of hydrogen adsorption at low temperatures (193° K) caused by the slow rate of the process.

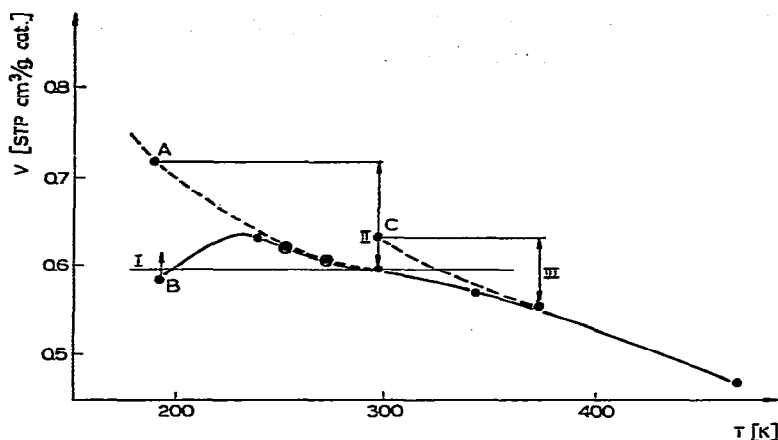


Fig. 5. Results of hydrogen adsorption: I = the amount of additional sorption after moving from point B (sorption on a "clean" surface at 193° K) to ambient temperature; II = the additional sorption after moving from ambient temperature to 193° K (point A was obtained by summing the sorption value at ambient temperature and the additional sorption at 193° K); III = the additional sorption after moving from 373° K to ambient temperature (point C was obtained similarly to point A in moving from 373° K to 298° K).

The contact time of hydrogen with iridium under the conditions of the method used is relatively short. Increase of temperature is accompanied by a faster hydrogen adsorption on the iridium surface. Therefore, the reverse process, *i.e.*, passage from higher to lower temperatures, does not result in barriers of a kinetic character. Thus the position of point A would be a natural consequence of the hydrogen sorption ability being increased by the iridium surface as the temperature of the system decreases. The difference between the positions of points A and B may be a measure of the non-equilibrium character of the adsorption process at low temperatures.

Since Fig. 3 suggests that the three types of hydrogen adsorption successively attain their sorption maxima, it is expected that any individual type should behave analogously to that described above. Such an interpretation of the measurements points to the non-equilibrium character of the curve in Fig. 3 starting close to 393° K and moving in the direction of lower temperatures. Similar non-equilibrium behaviour of hydrogen adsorption at low temperatures was observed for nickel¹⁴ and platinum³.

The occurrence of physical adsorption of hydrogen on iridium at low temperatures may result in the slight hydrogen thermodesorption mentioned earlier. Under conditions of thermodesorption, two processes of a completely different type may

occur. (1) An increase in the rate of hydrogen chemisorption with increasing temperature. (2) Thermodesorption of previously weakly adsorbed hydrogen takes place with increasing temperature. The rate of the second process is probably slightly larger than the rate of the first, accounting for the slight thermodesorptive effects observed.

Oxygen sorption

Measurements of oxygen adsorption on the clean surface of iridium were carried out within a similar temperature range to that used for hydrogen (193–773° K), occasionally at a temperature of 973° K. The results are presented in Fig. 6. Curve I was obtained for a 5% iridium catalyst, curve II for a 3% iridium catalyst. The methods of obtaining the two curves were slightly different.

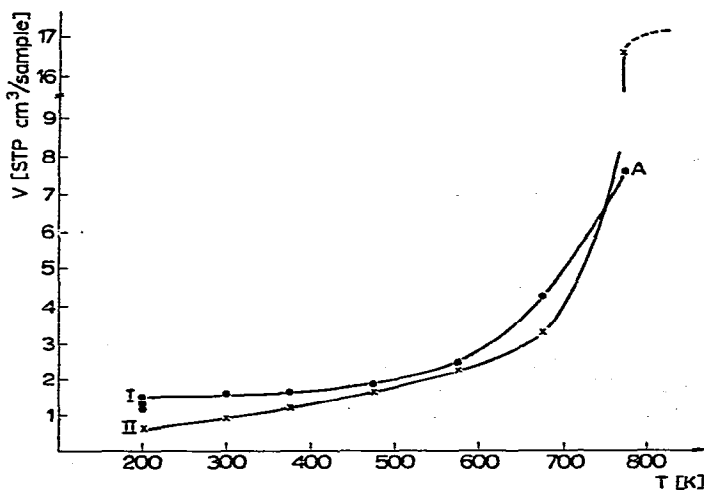


Fig. 6. Oxygen sorption as a function of temperature (II, 5% iridium catalyst; I, 3% iridium catalyst). Point A corresponds to complete sorption of the injections.

Curve I was constructed from successive measurements of oxygen sorption at gradually increasing temperatures. The results of the measurements were reproducible up to 573° K (see Fig. 6). At 673° K the heights of successive recordings of the first chromatographic peaks (responses of a detector to oxygen) were not constant. The heights of the second peaks attained constancy at lower temperatures. At 773° K *ca.* 40–50% of the oxygen was rapidly and irreversibly sorbed, and the height of the chromatographic peaks were then increased only slowly. Despite many injections, the height of the peaks did not attain constancy. Thus, in all subsequent measurements at $\geq 773^\circ \text{K}$, oxidation in a stream of oxygen was used and the amounts of the gas sorbed were determined by hydrogen titration at 773° K.

Curve II was obtained in a similar manner up to 298° K. At this temperature, the temperature was gradually increased, only maintaining the temperature constant during each measurement. In this way the amounts of oxygen sorbed in subsequent measurements were added to the amount sorbed at ambient temperature. Such a treatment made reproduction of results impossible.

The method proposed above was based on the assumption (confirmed experimentally) that there were no oxygen thermodesorptive effects within the range of temperature used. At 773° K, the difficulty in attaining constancy of peaks heights was again observed.

Fig. 6 indicates that both curves follow similar courses. The monotonic growth in oxygen sorption with increasing temperature makes it difficult to ascribe the monolayer to any particular temperature range. However, it is clear that near ambient temperature the growth is relatively slow. It can be assumed that oxygen, under these conditions, does not significantly penetrate the bulk of the metal and covers its surface with an approximate monolayer. The amount of oxygen adsorption (Fig. 6, curve I) was reproducible for the established catalyst surface at temperatures up to 573° K.

The rapid increase in sorption above 673° K is most probably due to bulk oxidation of iridium and the slow growth of the chromatographic peaks points to the fact that this process is somewhat hindered at its final stage. It appears that the measurements of the bulk oxidation of the iridium catalyst cannot be obtained reproducibly. This is demonstrated in Table I for a catalyst containing 5 wt % of iridium. Although the time of contact of the catalyst with oxygen, and later the temperature, is increased the amount of oxygen sorption (determined by the amount of hydrogen required in its titration at 773° K) decreases, but never below 60% of the maximal value (Table I). Strong processes of sintering accompanying the measurements are most likely to be responsible for this effect.

TABLE I

THE EFFECT OF SUBSEQUENT DIFFERENT METHODS OF OXIDATION ON THE AMOUNT OF IRIIDIUM OXIDIZED

<i>Method of oxidation</i>	<i>Amount of hydrogen used for titration at 773° K (cm³ at STP per g of catalyst)</i>
1 By injection at 773° K	19.63
2 30 min in a stream of oxygen at 773° K	20.77
3 130 min in a stream of oxygen at 773° K	17.82
4 1020 min in a stream of oxygen at 773° K	17.15
5 30 min in a stream of oxygen at 973° K	14.74
6 45 min in a stream of oxygen at 973° K	12.93

Sintering, in the case of iridium, is such an effective barrier for complete bulk oxidation that even a higher temperature and long contact with oxygen cannot overcome this effect. The occurrence of sintering is demonstrated by a considerable decline in the activity of the metal surface, *e.g.*, for a 1% iridium catalyst, the amount of hydrogen chemisorption at the end of the measurements was 15 times less than at the start.

The amount of oxygen sorbed also appears to be a function of the time of a contact with the catalyst, as illustrated in Table II for a catalyst containing 1% of iridium. These results might be due to the effect of exchange between surface iridium atoms and adsorbed oxygen to form a subsurface oxide phase. This phase is unlikely to be reduced by hydrogen at ambient temperature and therefore its presence ac-

TABLE II
OXYGEN SORPTION FOR A 1% IRIIDIUM CATALYST AT 298 °K

No.	Time of contact with oxygen at 298 °K	Amount of hydrogen (cm ³ at STP) used for		Total amount of H ₂ (cm ³ at STP)	Amount of O ₂ corresponding to H ₂ from column (cm ³ at STP)	Amount of O ₂ from chemisorption (cm ³ at STP)
		Titration of oxygen at 298 °K	Additional titration with hydrogen at 773 °K			
1	adsorption on a "clean" surface	3.4	0.22	4.47	2.24	2.69
2	11 titration cycles	—	2.34	—	—	—
3	20 min in a stream of O ₂	2.47	2.86	5.33	2.26	2.79
4	60 min in a stream of O ₂	2.21	5.57	8.64	4.32	—
5	720 min in a stream of O ₂	1.1	6.45	7.55	3.78	2.62

counts for the decrease in reactivity of oxygen with increasing time of contact with the metal surface (column 3, Table II).

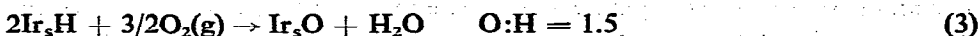
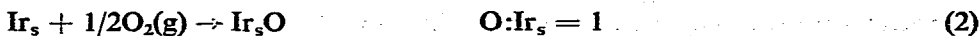
Oxygen reacting with hydrogen at 298° K might come from part of the gas adsorbed on the surface, the amount involved in the complete sorption would decrease with the growth of the oxide phase. The remaining part of the oxygen adsorbed by the subsurface layer of the metal (oxide phase) would be less reactive and its amount would correspond to the result of the titration with hydrogen at 773° K.

The increasing values in column 4 of Table II might be due to the growing amount of oxygen in the oxide layer with the time of oxidation. The initial, very low result in this column can be easily explained by the slow course of the site exchange, which after oxygen adsorption hardly occurred at all. The values in column 5 grow as expected for the increasing amount of oxygen adsorbed.

It appears that the increasing temperature up to 773° K of a catalyst oxidized at 298° K, and its later re-oxidation at 298° K after having been cooled, results in a reconstruction of the metal surface corresponding to *ca.* 20% of the initial oxygen adsorption. In the light of our investigations and literature data⁶ mentioned earlier, this phenomenon is not connected with oxygen desorption from the surface, but with formation of an oxide phase of the metal.

Oxygen-hydrogen interactions on iridium catalysts: determination of the dispersion of the metallic phase

Interactions between hydrogen, oxygen and Ir-Al₂O₃ are shown in eqns. 1-4 described by Brooks⁴



Within the temperature range used for hydrogen and oxygen adsorption, titrations of previously adsorbed hydrogen with oxygen and of previously adsorbed oxygen with hydrogen were examined. The results are presented in Fig. 7 as a function of temperature for a 1% iridium catalyst. The decreasing values obtained with an increasing number of titration cycles at individual temperatures seem to be due to two processes. (1) Sintering of a catalyst during the measurements, this process being probably greater at higher temperatures. (2) The influence of water formed as a result of titration according to eqns. 3 and 4, this being greater at lower temperatures.

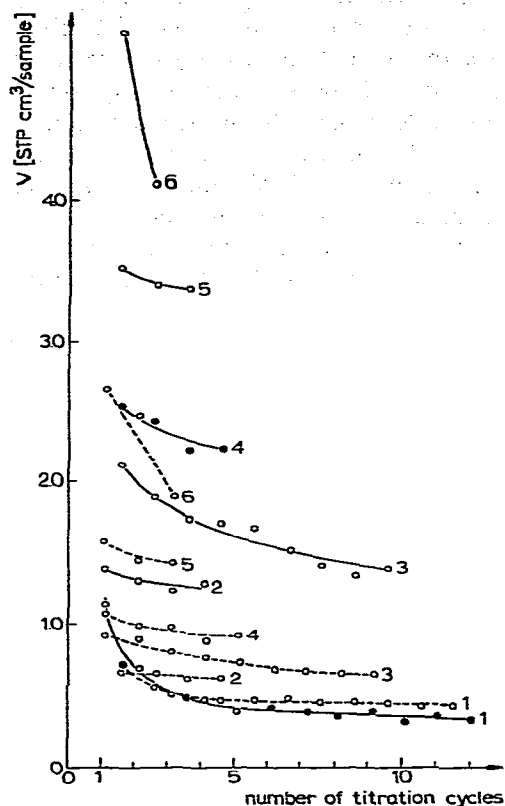


Fig. 7. Titrations on a 1% iridium catalyst at different temperatures. Dashed curves correspond to the oxygen results, full curves to the hydrogen results. Curves: 1 = 298 °K, 2 = 373 °K, 3 = 473 °K, 4 = 573 °K, 5 = 673 °K, 6 = 773 °K.

Water is likely to have an important influence on the results of sorption measurements during the titrations in curves 1–5. The process of blocking of the metal surface by water seems to occur selectively, *i.e.*, a part of the surface is more sensitive to the presence of water, probably that part in contact with the support. This is borne out by the initially large but subsequently smaller decrease in values observed. The constancy of the final values also indicates that part of the surface is not subject to blocking by water. The decrease in values as a function of the number of titration cycles is not connected with sintering, since the amount of hydrogen ab-

sorption on the clean surface obtained after titration was the same as that obtained before the titration. There is no doubt about the interpretation of the fast decrease in values at 973° K, which is due to fast sintering of the metal surface. After a series of tests within the temperature range 773–973° K carried out on a 1% iridium catalyst, we observed the hydrogen adsorption on the clean metal surface to decrease to very low values.

Fig. 8 illustrates similar titrations for a 5% iridium catalyst at 298° K. A decrease of up to 30% of the initial value can be seen as a function of the number of titration cycles, and the ratio of hydrogen to oxygen consumed in the reaction is 2. Since similar results were also obtained for a 3% iridium catalyst, it is surprising that the ratio of hydrogen to oxygen for the 1% iridium catalyst at 298° K is close to 1 (curve 1, Fig. 7). It is difficult to interpret this fact. Only an oxygen spillover effect could completely account for the phenomenon. However, the assumption of such a large effect at ambient temperature is debatable in the light of literature data¹⁵.

The comparability of titration results for different metals in Group VIII has been examined and rhodium, for example¹¹, was found to exhibit similar behaviour to iridium. In the present Figures, titration results at 193° K are not presented since at this temperature hydrogen does not react with the oxidized surface. Instead, the reverse reaction occurs, *i.e.*, oxygen is sorbed on a reduced surface but the amount involved is less than that expected.

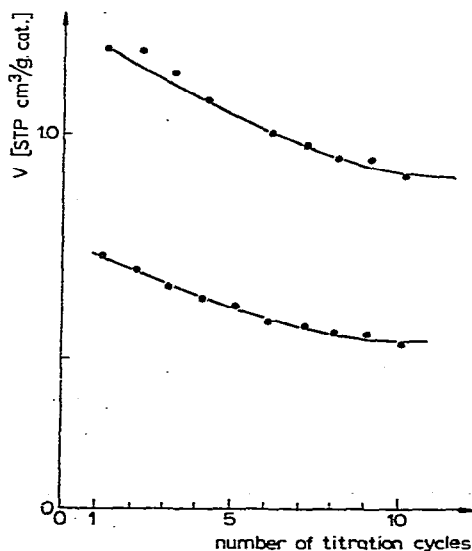


Fig. 8. Results of titration on a 5% iridium catalyst at 298 °K.

The problem connected with the ratio of oxygen adsorbed on a clean surface to that of hydrogen is of practical importance in estimating the iridium dispersion (yielding the stoichiometry of interaction). Fig. 9 presents curves for oxygen and hydrogen adsorption on the clean surface. Since the curves are not horizontal over any temperature range we should not expect the formation of a monolayer at any temperature. However, comparability of the hydrogen and oxygen results at tem-

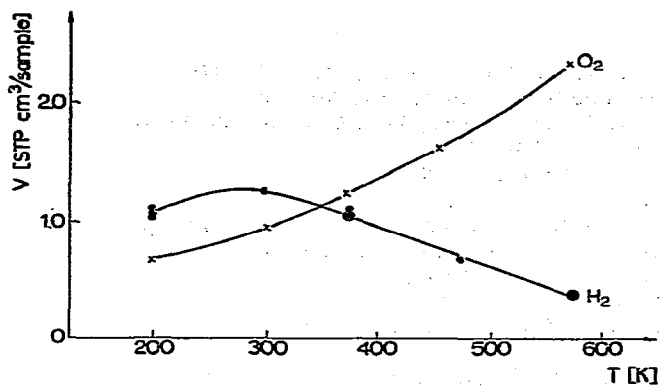


Fig. 9. The results of oxygen (x) and hydrogen (●) chemisorptions on a 5% iridium catalyst.

peratures close to ambient allows a determination of the iridium surface. Values of the hydrogen to oxygen ratio at 298° K 1.26, 1.27 or 1.2 for 1, 3 or 5% catalysts, respectively. Greater adsorption of H₂ than of O₂ at ambient temperature was observed elsewhere⁴. For a 1% iridium catalyst 298° K we have observed that reversible hydrogen sorption comprises 5–10% of the total sorption (upon flushing the catalyst with carrier gas for 15–60 min and measuring the adsorbed hydrogen). Taking into account reversible hydrogen adsorption during hydrogen chemisorption, it may be concluded that at ambient temperature the values of the stoichiometries of the surface interactions in the iridium–oxygen and iridium–hydrogen systems are similar.

It is generally believed⁴ that the stoichiometries of hydrogen–metal systems are equal to one (see eqn. 1), so that we can conclude that the stoichiometries of the interactions of oxygen and hydrogen with the iridium surface not only approximate each other but are also close to one. It was found that the dispersion is influenced by keeping the catalyst at temperatures higher than 773° K. Thus, an oxidized 5% iridium catalyst kept for several minutes at this temperature suffered a reduction in its surface of *ca.* 30%. The results of dispersion measurements for a catalyst containing 5% of iridium are shown in Table III. The values are in good agreement.

Therefore, despite of the uncertainty as to the stoichiometry of the oxygen and hydrogen interactions with the iridium surface, measurements of the chemisorption and titration in this system seem to be useful for the determination of the iridium dispersion.

TABLE III

COMPARISON OF THE METHODS OF DETERMINATION OF THE IRIIDIUM DISPERSION

<i>Method of dispersion measurement</i>	<i>Dispersion (%)</i>
From H ₂ chemisorption	34.0
From O ₂ chemisorption	24.5
From H ₂ titration of the oxidized surface ¹	28.8
From O ₂ titration of the reduced surface	31.0

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