

CHROM. 11,228

INTERACTIONS BETWEEN OXYGEN, HYDROGEN AND SUPPORTED RHODIUM OVER A WIDE TEMPERATURE RANGE

I. OXYGEN AND HYDROGEN ADSORPTION

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(First received November 22nd, 1977; revised manuscript received May 25th, 1978)

SUMMARY

Interactions of oxygen and hydrogen with the surface of rhodium-alumina catalysts within the temperature range -80 to 700° were examined by pulse gas chromatography. Oxygen and hydrogen chemisorptions were carried out on "clean" rhodium surfaces and titrations of the oxidized surface with hydrogen were performed together with those of the inverse reaction, *i.e.*, titration of the reduced surface with oxygen.

In spite of many problems which are discussed, the results of oxygen and hydrogen chemisorption at ambient temperature can be used for the determination of the surface area of rhodium. It was found that above 200° oxygen considerably penetrated the rhodium lattice forming stable suboxides, and above 500° the product of oxidation was rhodium(III) oxide (Rh_2O_3).

INTRODUCTION

In spite of many problems, chemisorption methods for the determination of the surface area of metals dispersed on supports are commonly used. A knowledge of the stoichiometry of surface interactions between a metal and an adsorbate is desirable when applying adsorption methods and this constitutes a problem. The choice of surface stoichiometry, measurement conditions and the pre-treatment of catalysts before measurements is arbitrary. Therefore, further adsorption investigations of metal-adsorbate systems, from the point of view of their usefulness for the determination of metal dispersions, seemed desirable. Previous adsorption investigations dealt mainly with platinum¹⁻⁹ and only a few concentrated on other metals from Group VIII of the periodic system¹⁰⁻¹⁶.

In order to determine the degree of dispersion of rhodium deposited on supports (usually alumina and silica) the adsorptions of oxygen, hydrogen and carbon monoxide have been used, together with the reaction of gas titration of the previously adsorbed oxygen and hydrogen^{9,17-20}.

Most of the investigations were carried out under static conditions, and only few under dynamic conditions^{9,20,21}. In this work, pulse gas chromatography was used for chemisorptive investigations of oxygen and hydrogen on rhodium catalysts supported on alumina over a wide temperature range (-80 to 700°).

EXPERIMENTAL

Equipment

The measurements of gas adsorption were carried out in the apparatus (previously described^{12,22}) used for pulse gas chromatography. In previous papers we described a procedure for the careful purification of the carrier gas (argon) and oxygen and hydrogen adsorbates^{22,23}. An amount of *ca.* 2–3 g of catalyst was placed in a glass reactor which, by welding with a gas burner, was joined to the measurement system before pre-treatment of the catalyst.

Catalyst

We used rhodium catalysts containing 0.5–4% of a metal deposited on alumina by an impregnation method. The catalysts were prepared by means of impregnation of the support with an aqueous solution of rhodium(III) nitrate. The contents were evaporated under vacuum (3–4 h), then dried at 105° (16 h) and reduced with a stream of electrolytic hydrogen (20 cm³/min) at 500° for 16 h. After cooling in a stream of hydrogen the product was stored. The conditions for the pre-treatment of catalysts and measurement conditions are presented in Part II²⁸.

RESULTS AND DISCUSSION

Preliminary investigations

In order to determine the conditions for the pre-treatment of catalysts before the adsorption measurements we measured the influence of the time of reduction at 500° of a catalyst containing 4% of rhodium on the results of hydrogen and oxygen adsorption at ambient temperature. The results are given in Fig. 1. The results are nearly constant (within $\pm 5\%$ of the average values) and do not depend on the time of the catalyst reduction.

These results permit the conclusion that the reduction at 500° , even if the catalyst has previously been oxidized at room temperature, is fast and results in reproducible sorptive properties of the metal surface. The surface was considered to be "clean" if it showed constant and reproducible adsorptive properties, realizing of course the more or less conventional character of the concept of a "clean" surface.

For measurements the time of reduction (30 min) or pulse reduction (tens of hydrogen injections) was used. With fresh catalysts a 2 h reduction was used after their previous drying in a stream of carrier gas (2–3 h) at 500° .

The results of influence of the time of passing a carrier gas through a 4% rhodium–alumina catalyst at 500° on the adsorption results are presented in Table I. The results of oxygen adsorption reveal a slight decrease (10%) within a degassing time range of 0.1–3.0 h. A considerable decrease in oxygen adsorption (*ca.* 30% of the initial value) is observed after a degassing time of 16 h.

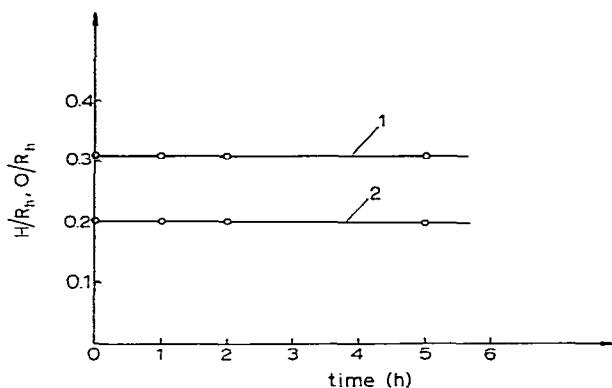


Fig. 1. Influence of time of reduction at 500° on oxygen (1) and hydrogen (2) absorption at ambient temperature for 4% Rh-Al₂O₃ catalyst.

TABLE I

INFLUENCE OF THE TIME OF OUTGASSING (AT 500°) ON OXYGEN ADSORPTION (AT 25°)

<i>Time of outgassing (h)</i>	<i>Oxygen adsorption [cm³ (STP) per g catalyst]</i>
0.1	0.70
0.5	0.68
1.0	0.65
3.0	0.63
16.0	0.44
0.5	0.66

The results agree with those obtained by Flynn and Wanke⁹, but we do not think that it is hydrogen left on the metal surface that is responsible for the decrease in oxygen adsorption. We consider that it may be the result of the re-oxidation of metallic rhodium at 500° with oxygen from the alumina support. The amounts of hydrogen equivalent to such a large decrease in oxygen adsorption seem too large (see Fig. 3). However, one should also take into consideration other possible impurities that could diffuse from the support on to the metal surface.

In pre-treatment stage rhodium catalysts were washed with carrier gas for 1 h at 500° after their reduction.

A high degree of possible participation of reversible hydrogen adsorption on the metal surface made us measure the dependence of hydrogen adsorption on the flow-rate of the carrier gas. The results of the measurements for a 1% rhodium-alumina catalyst at ambient temperature are presented in Fig. 2. Reversible hydrogen adsorption seems to be responsible for the considerable initial decrease in hydrogen adsorption. The hydrogen adsorption for a volume flow-rate of 300 (STP) cm³/min is smaller and could result from too short a contact of hydrogen pulses with the metal surface.

Within the volume flow-rate range of 25–150 (STP) cm³/min the results of

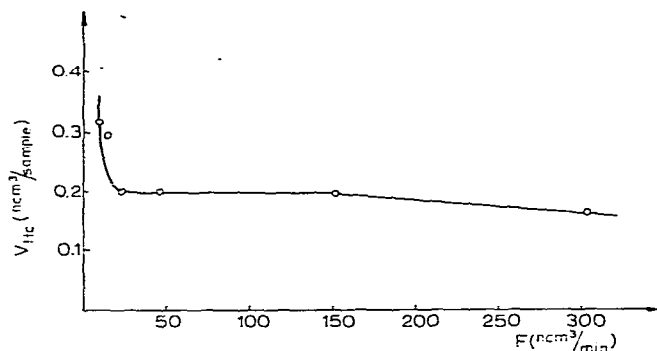


Fig. 2. Influence of flow-rate of carrier gas on hydrogen adsorption at ambient temperature for 1% Rh-Al₂O₃ catalyst. $\text{ncm}^3 = \text{cm}^3$ (STP).

hydrogen adsorption are roughly constant. This was the reason why a volume flow-rate of 40 (STP) cm^3/min was chosen for further measurements.

In the course of preliminary measurements the behaviour of an alumina support in relation to oxygen and hydrogen was examined within the temperature range -80 to 700° . The observed adsorption effects were virtually insignificant, but the support is not certain to be passive in the presence of a metal, which is an active component (as it was in the absence of a metal).

In the literature there are suggestions that, especially at high temperatures, processes of transportation of an adsorbate from a metal on a support can take place (spillover processes²⁴). An inverse process, for instance migration of oxygen or hydroxyl groups from a support on a metal, is also said to be possible.

Hydrogen chemisorption

Hydrogen as an adsorbate is subject not only to fast and irreversible adsorption on a metal surface but also to a reversible (slower) adsorption, the participation of which is considerable (often tens percent of the total hydrogen sorption^{1,21}). The above feature of hydrogen should be considered particularly in relation to the conditions of a pulse dynamic method which is suitable for investigations of fast and irreversible adsorption processes. The technique of pulse gas chromatography has frequently been used for measurements of hydrogen adsorption on the metals of the platinum group^{14,25}.

As follows from Fig. 2, a considerable participation of reversible hydrogen sorption can be expected at low volume flow-rates of carrier gas [below 20 (STP) cm^3/min]. The results of hydrogen adsorption for two catalysts (1% and 4% rhodium) as a function of temperature are presented in Fig. 3.

The hydrogen adsorption decreases considerably as the temperature increases from -80 to 600° . At ambient temperature no clear plateau on the hydrogen adsorption curve was observed as Wanke and Dougharty¹⁷ suggested in work in which rhodium-alumina catalysts were examined under static conditions.

The results of hydrogen adsorption under the conditions of pulsed gas chromatography are reproducible if the catalysts are not subject to temperatures above the preliminary reduction temperature (see Fig. 3). A catalyst containing 4% of

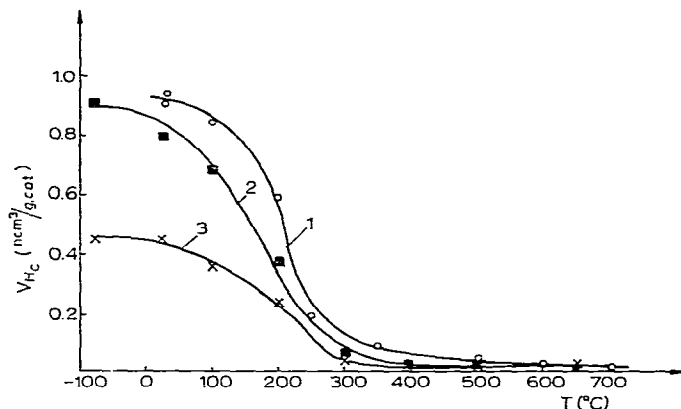


Fig. 3. Dependence of hydrogen adsorption on the temperature. (1) 4% Rh-Al₂O₃ catalyst; (2) 4% Rh-Al₂O₃ catalyst after 16-h sintering in oxygen at 700°; (3) 1% Rh-Al₂O₃ catalyst.

rhodium calcined in oxygen (16 h) at 700° gave lower hydrogen and oxygen adsorptions (Figs. 3 and 4).

On the basis of the results in Fig. 3 it is difficult to choose a temperature of hydrogen adsorption that would be suitable for the determination of the metallic surface area of rhodium dispersed on alumina. Such a behaviour of the system permits the conclusion that the stoichiometry of the rhodium-hydrogen surface interactions decreases monotonically as the temperature increases.

Oxygen adsorption

Oxygen as an adsorbate under the conditions of pulse gas chromatography has the particularly advantageous feature that its adsorption on the surface of a metal belonging to the platinum group is, in fact, a fast and irreversible process over a wide temperature range.

There is also some disadvantage in using oxygen adsorption for the determination of the area of a metallic surface, namely the problem of sorbing oxygen into the surface layers of the metal²⁶. The surface reveals further sorptive properties that apparently increase the surface stoichiometry of the metal-oxygen system.

The results of oxygen adsorption on rhodium-alumina catalysts are presented in Figs. 4 and 5.

On the basis of such behaviour of the oxygen-rhodium system, three temperature ranges can be distinguished:

(I) -80 to 200°, within which adsorption of oxygen on rhodium seems to be a surface process although the participation of the sorption of oxygen in the surface layers of a metal increases with increase in temperature:

(II) 200-500°, within which the drastic increase in oxygen sorption results from the process of rhodium bulk oxidation;

(III) above 500°, within which range the process of complete oxidation takes place and the oxide structure of rhodium with a constant quantitative composition is formed.

The behaviour of the rhodium-oxygen system is similar to that of the palladium-oxygen system which we previously examined²².

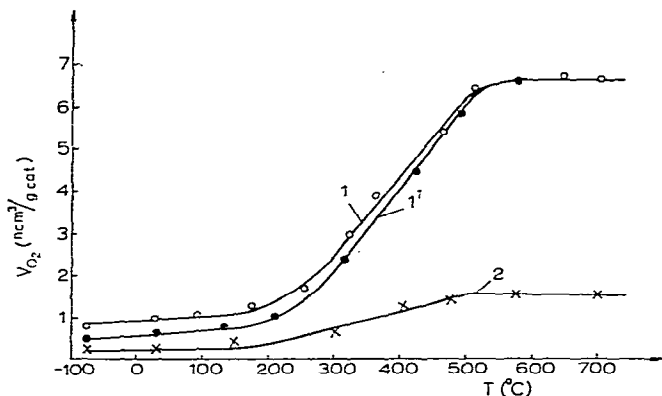


Fig. 4. Dependence of oxygen adsorption on temperature. (1) 4% Rh-Al₂O₃ catalyst; (1') 4% Rh-Al₂O₃ catalyst after sintering; (2) 1% Rh-Al₂O₃ catalyst.

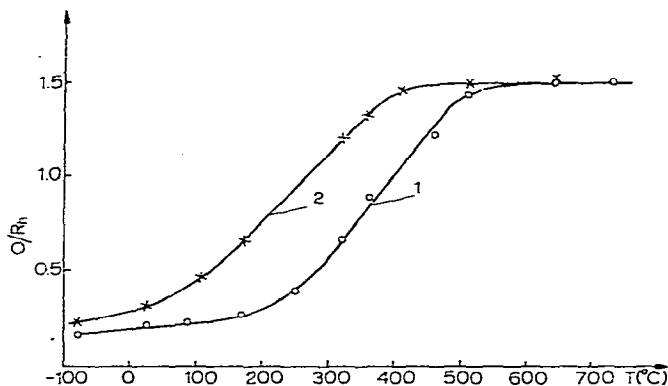


Fig. 5. Influence of method of oxidation on oxygen adsorption for 4% Rh-Al₂O₃ catalyst. (1) Pulsed oxidation; (2) oxidation with a stream of oxygen for 15 h.

Fig. 5 presents the results of oxygen sorption measured by the pulse method. It also contains the results of the oxidation of a catalyst sample for 15 h with a stream of oxygen at a volume flow-rate of 20 (STP) cm³/min.

It follows from Fig. 5 that the curve for continuous oxidation (2) within the temperature range -80 to 500° lies above the curve for pulsed oxidation (1).

The oxygen adsorption at -80° corresponding to continuous oxidation was determined by heating the sample (after it had been washed with carrier gas) to 500° and titrating it with hydrogen. Such a procedure was justified by the incomplete reduction of the oxidized rhodium surface at -80° .

The increasing difference between curves 1 and 2 (Fig. 5) as the oxidation temperature increased can be explained by sorption of oxygen into the internal layers of the metal. The results of curve 2 were established earlier than those of curve 1 (ca. 400°). At temperatures higher than 500° bulk oxidation is so fast that the method of rhodium oxidation has in fact no significance. It is worth stressing that

over the whole temperature range during pulsed oxidation a sample, once oxidized, did not reveal further sorptive properties at a given temperature, no matter how long it was washed with carrier gas. This indicates that oxygen adsorption on rhodium is a fast and irreversible process over the whole temperature range and is not accompanied by oxygen desorption from rhodium into the gaseous phase. The difference between curves 1 and 2 (Fig. 5) seems to be caused by a promoting influence of oxygen pressure in the gaseous phase on the reconstruction of the metal surface during its oxidation.

Flynn and Wanke⁹, however, considered the possibility of the presence of reversibly bonded oxygen on rhodium-alumina at ambient temperature. They also assumed the possibility of an effect of local heating of a metal evoked by fast adsorption from a stream of pure oxygen.

It is possible that the effect of local heating of a metal influences considerably the results of fast oxygen adsorption. Nevertheless, the assumption of the desorption of the reversibly adsorbed oxygen on platinum and rhodium surfaces at ambient temperature seems improbable.

A sample, once oxidized, did not undergo further adsorption (to an extent greater than 2% of the initial value) on washing with carrier gas for several hours. Therefore little secondary adsorption could result either from earlier oxygen desorption or from its sorption into the internal sub-surface layers of a metal.

With platinum at higher temperatures (up to 600°) one observes some participation of oxygen desorption from the platinum surface into the stream of carrier gas²⁵.

No influence of the volume of dosed oxygen pulses (0.32–1.27 cm³) on the extent of oxygen adsorption on rhodium at ambient temperature was noticed. This may imply a lack of influence of the exothermic effect accompanying oxygen adsorption on the extent of the adsorption. The effect should be seen better the greater is the volume of a dosed oxygen pulse. It is more likely that the effect will be detected under static rather than dynamic conditions.

Oxygen adsorption at ambient temperature was found to be slightly lower (up to 10%) than that calculated from hydrogen titration at 600°. Before the titration the sample was degassed for 1 h in a stream of argon and heated to the temperature of the hydrogen titration, *i.e.*, 600°.

The results of several successive measurements are presented in Table II. The last column shows the difference between the results, which is equal to *ca.* 9% of the oxygen adsorption value at ambient temperature. Two possible explanations for the differences seem to be justified: firstly hydrogen adsorption at 600°, and secondly re-oxidation of the rhodium metallic phase. The re-oxidation could occur indirectly through dissociable adsorption of water originating from hydrogen titration at 600° on the rhodium surface²⁷. The process could result in the desorption of hydrogen atoms in the form of molecules after earlier recombination. The process could be a secondary one in relation to the primary titration and it would be encouraged by the participation of the alumina support which, even at 600°, keeps water on its surface for a long period. The possibility of adsorption of water on rhodium has been discussed²⁷.

The reproducibility of the sorptive properties of oxygen on rhodium is readily observed, when the temperature of a sample is increased to 600° after earlier oxygen

TABLE II

RESULTS OF OXYGEN ADSORPTION AT 25° (A) AND TITRATION WITH HYDROGEN AT 500° (B) FOR 4% Rh-Al₂O₃ CATALYST

Number of cycle	O/Rh (A)	O/Rh (B)	O/Rh (A) - O/Rh (B)	
			O/Rh (A) (%)	
1	0.23	0.25	8.7	
2	0.23	0.25	8.7	
3	0.32	0.24	9.1	
4	0.23	0.25	8.1	
5	—	0.36 (a)*	—	
6	—	0.36 (b)*	—	
7	0.23	0.25	8.7	
8	0.23	0.25	8.7	

* These results were calculated from titration with hydrogen at 500° after previous oxidation with a stream of oxygen at 25° for (a) 15 h and (b) 1.5 h.

adsorption (O_c)₁ at ambient temperature. Then additional oxygen adsorption (O_c)_n follows after cooling the sample to ambient temperature. The procedure is illustrated by Table III.

From Table III it follows that the increase in temperature to 600° in the first cycle allows the reproduction of almost half (48%) of a surface. In subsequent cycles 38% and 23% of the surface was reproduced.

The above behaviour might have been determined by the thermal desorption of the reversibly adsorbed oxygen, particularly on increasing the temperature⁹. This possibility is disproved by the results of hydrogen titration at 500° after the cycles of oxidation at 25° were completed. The hydrogen results imply an even higher degree of oxidation of the sample (ca. 20%). It could be caused by the additional oxidation indicated in Table II.

The results in Tables II and III seem to disprove the possibility of thermal desorption of oxygen but they confirm the fast and irreversible character of the sorption of oxygen within the investigated temperature range. Reconstruction of a surface under the influence of oxygen seems to be proved. Its efficiency increases with increase in temperature, even at 25° in contact with oxygen (Table II, cycles 5 and 6). The process contributes considerably to the increase in oxygen adsorption under pulsed conditions.

TABLE III

ILLUSTRATION OF THE RECONSTRUCTION OF OXYGEN ADSORPTION PROPERTIES ON RHODIUM SURFACE AFTER SUCCESSIVE CYCLES OF HEATING TO 600° (CATALYST 4% Rh-Al₂O₃)

The results of oxygen chemisorption are expressed as O/Rh.

	O_{c_1}	O_{c_2}	O_{c_3}	O_{c_4}	ΣO_c	$O_c = \frac{H_T(600^\circ)}{2}$	$\frac{O_c - \Sigma O_c}{\Sigma O_c} (\%)$
I	0.23	0.11	—	—	0.34	0.41	+ 21
II	0.23	0.11	0.087	0.053	0.48	0.57	+ 19

Hence the choice of a temperature of oxygen adsorption suitable for the determination of the surface area of rhodium must be arbitrary although a low temperature (up to *ca.* 25°) should be selected. If strongly dispersed rhodium catalysts ($D > 0.8$) are being investigated, the temperature of oxygen adsorption will probably not be of great importance, as it leads to complete oxidation of the rhodium metallic phase. (D is the ratio of the number of metal surface atoms to the total number of metal atoms dispersed on the support.)

In our opinion, the rhodium–oxygen and palladium–oxygen systems²² differ considerably from the platinum–oxygen system²⁵ at temperatures above 200°. The behaviour of the platinum–oxygen system reveals features of surface oxidation²⁵ corresponding to the formation of several surface monolayers of oxygen. Metals such as rhodium and palladium and probably iridium, ruthenium and rhenium undergo bulk oxidation to the respective oxides. The process can take place only if the temperature is sufficiently high and the metal is not sintered too much. In other cases the oxidation process could be restricted by the size of the surface limiting the rate of the process. This probably occurred in the work described by Wanke and co-workers^{17,18}. Rhodium deposited on a carrier undergoes bulk oxidation more easily as its dispersion value increases. At temperatures above 500° rhodium changes into rhodium(III) oxide (Rh₂O₃). The above suggestion is supported by Table IV, which gives results for the oxidation of rhodium catalysts at temperatures above 500°.

The oxidation was carried out either by the pulse method (a) or with a stream of oxygen of volume flow-rate *ca.* 40 ncm³/min (b). Some of the results were ob-

TABLE IV
RESULTS OF RHODIUM OXIDATION IN THE RANGE 500–700° FOR Rh–Al₂O₃ CATALYSTS

<i>Proportion of rhodium (%)</i>	<i>Temperature of oxidation (°C)</i>	<i>O/Rh</i>	<i>Method of oxidation*</i>
0.5	600	1.60	a
		1.51	c
		1.59	b (16 h)
1.0	500	1.47	a
		1.45	c
		1.52	a
	630	1.45	c
		1.50	b (1 h)
		1.56	a
3.0	670	1.52	c
4.0	500	1.48	a
		1.51	b (40 h)
		1.57	a
	630	1.57	b (15 h)
		1.52	
700	1.58	a	
		1.53	c

* a, Pulse method of oxidation; b, stream oxidation (degree of oxidation was estimated by means of the pulse method of titration with hydrogen); c, pulse method of oxidation (O/Rh obtained as in b).

tained by titrating the oxidized sample with hydrogen (c). Within a range of $\pm 5\%$ of the average values, all of the methods gave similar results.

From Table IV, it follows that at temperatures above 500° rhodium is completely oxidized to rhodium(III) oxide. There is a slight but visible tendency for the formation of some oxide structures with a higher degree of oxidation. This can be explained by assuming that partial re-oxidation of the alumina carrier occurs at these temperatures.

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