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

### II. TITRATION REACTIONS IN THE OXYGEN-HYDROGEN SYSTEM AND EVALUATION OF DISPERSION OF RHODIUM-ALUMINA CATALYSTS

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#### SUMMARY

The application of the results of titration in the oxygen-hydrogen system to the determination of metal surface areas seems to be influenced by water, the product of the titration process. The dependence of the titration results on the number of successive titration cycles is discussed in terms of a proposed blocking mechanism, according to which water from the support gradually blocks part of the metal surface. The results of hydrogen and oxygen chemisorption and hydrogen-oxygen titrations are compared with respect to rhodium surface area determinations.

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#### INTRODUCTION

Gaseous titrations of previously chemisorbed hydrogen with oxygen and oxygen with hydrogen are commonly used in investigations of the degree of metal dispersion by adsorption methods. One of the main advantages of the titration method is that the metal surface need not be cleaned. It is well known that this "cleaning" is very troublesome and often requires drastic temperature conditions, resulting in sintering of the strongly dispersed metal. The titration method has, however, some disadvantages. The stoichiometry of the interactions between oxygen, hydrogen and a metal surface in adsorption investigation is not certain. Also, water formed during the reaction may have an adverse influence.

The preparation of the catalysts, the methods of measurement and the preliminary investigations were described in Part I<sup>1</sup>. The reactions of the gaseous titration occurred over a wide temperature range (−80 to 700°).

When the influence of water (steam) from the exterior on the results of titrations was investigated a special device was attached to the apparatus, as described elsewhere<sup>2,3</sup>, which allowed the saturation of the carrier gas. The amount of water (steam) dosed was regulated by means of steam-saturated carrier gas passing through the catalyst sample.

## EXPERIMENTAL AND RESULTS

*Hydrogen-oxygen titration measurements*

Typical results of hydrogen titration of previously chemisorbed oxygen (upper curves) at ambient temperature and those of oxygen titration of the reduced surface (lower curves) as a function of the number of titration cycles are presented in Fig. 1. The results of oxygen ( $O_C$ ) and hydrogen ( $H_C$ ) chemisorptions are also given.

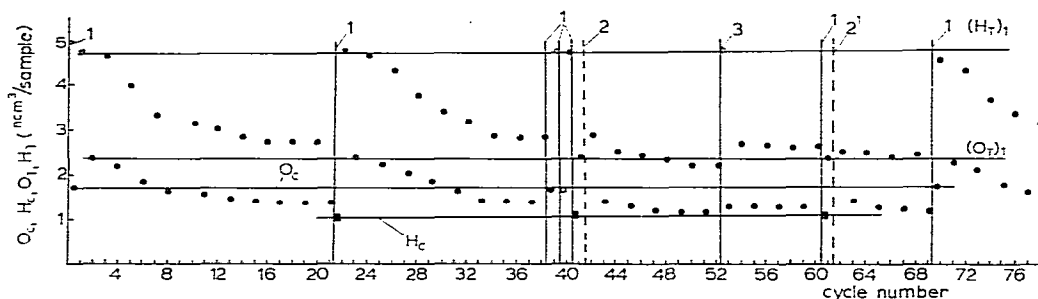


Fig. 1. Results of titration and chemisorption of oxygen and hydrogen. 1, Pre-treatment; 2 and 2', saturation with argon + water (steam) for 15 and 120 min, respectively; 3, washing with argon (16 h).  $\text{ncm}^3 = \text{cm}^3$  (STP).

The vertical full lines (1) determine the stage of catalyst pre-treatment before the measurement of oxygen or hydrogen chemisorption. The vertical broken lines (2) mark the stage of saturation of a catalyst sample with water introduced as steam in the stream of a carrier gas. The vertical full line (3) denotes washing of the sample (16 h) with carrier gas at ambient temperature.

From Fig. 1 it follows that the titration curves are dependent on the number of the cycles performed. At the beginning a considerable decrease in  $H_T$  and  $O_T$  values occurs and after 8–10 cycles the results are about 55% of the initial values. The behaviour of the system can be reproduced only if pre-treatment of a catalyst precedes the process.

The course of the titration curves ( $H_T$  and  $O_T$ ) could be explained if the metal surface area decreased during successive titrations. This seems improbable as the system completely reproduces its properties after the pre-treatment of a sample. Also, the stability of the results of oxygen and hydrogen adsorptions ( $H_C$  and  $O_C$ ) seems to discredit such a supposition. Another explanation is possible if we assume that during the measurements a gradual blockage of part of the metal surface (actually *ca.* 45%) occurs, and the blocked area does not participate in further titration reactions. As the number of titration cycles increases, there is more and more water in the system and thus the water might be the key to the whole problem. This supposition is confirmed by the results of titrations carried out after water has been introduced into the system (broken lines 2 and 2' in Fig. 1). The results depend only to a slight extent or not at all on the successive cycles of titration. Thus a justifiable conclusion could be drawn that if there is enough water in the system it will block a constant proportion of the surface of rhodium dispersed on alumina.

It seems that water formed during the titration reaction is desorbed from

the metal surface on to the alumina support. As the amount of water on the support increases it could react (possibly in the form of OH groups) with that part of the metal which is in direct geometrical contact with the support. In the process part of the surface is blocked and is unable to participate in the titration reactions. The other part of the rhodium surface, which is not subject to the possible action of water (OH groups) adsorbed on the support, would not be blocked and takes part in the titration reactions no matter how much water is adsorbed on the support. It must be stressed, however, that the amount of water in a sample under the chromatographic conditions is limited by both the temperature and other conditions of measurement.

Fig. 2 presents the results of titrations on the same catalyst (4% rhodium) as a function of successive measurement cycles at 25, 80, 160 and 240°. The catalyst had previously undergone many oxidations at 500–700° and its dispersion was 30% lower (Table I) than that of the catalyst for which measurement results are presented in Fig. 1.

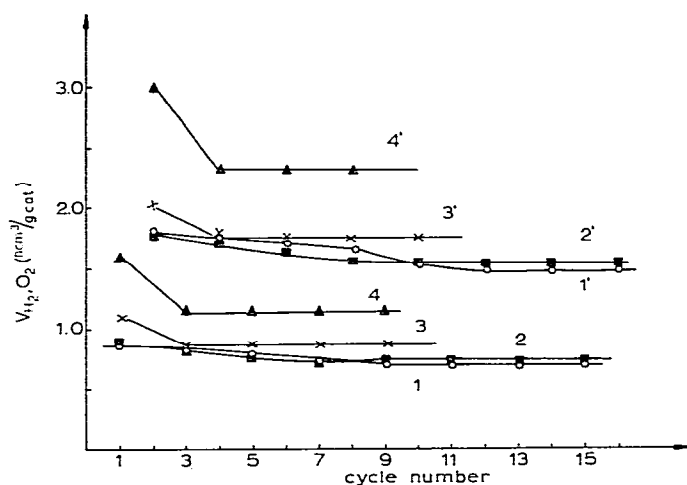


Fig. 2. Results of titrations: 1, 2, 3 and 4, titration with oxygen at 25°, 80°, 160° and 240°, respectively; 1', 2', 3' and 4', titration with hydrogen at 25°, 80°, 160° and 240°, respectively.

At 25° the titration curves are similar to those in Fig. 1 but the decrease is not more than 20% of the initial values.

For higher temperatures (160 and 240°) the decrease in the titration value is of the same order as that for lower temperatures, but it is observed only in the first two cycles as subsequent cycles give constant values. The behaviour of the titration curves in Fig. 2 seems to indicate a considerable dependence of rhodium surface blockage on the adsorbing power of a support sorbing water that is becoming smaller as the temperature increases.

The amount of water produced during one titration cycle within the range 25–240° is usually of the same order, no matter what the temperature. Hence, the conclusion could be drawn that stability of the surface properties of a support is

achieved faster the higher is the temperature determining the rate of the partial blockage of the metal surface. The area of the blocked surface does not depend on temperature, but rather on the extent of metal dispersion.

The results in Fig. 2 confirm the expected influence of the extent of rhodium dispersion on the decrease in titration results. The decrease in dispersion results in a smaller decrease in the titration results.

For a catalyst with a dispersion  $O/Rh = 0.31$  the decrease was about 45%. For the same catalyst after sintering ( $O/Rh = 0.21$ ) the decrease was about 20%. Water could be dissociatively adsorbed on the rhodium surface in accordance with eqns. 1 and 2<sup>4</sup>



The complete dissociation according to eqn. 1 seems more probable. However, it would not be the cause of the blockage of the rhodium surface, as the adsorbed oxygen and hydrogen atoms are natural products of both oxygen and hydrogen chemisorption and of hydrogen-oxygen titrations on the metal surface. The formation of unreactive hydroxyl groups on the rhodium surface (eqn. 2) would provide an explanation of the partial poisoning of the surface, if we assume the impossibility of their reduction at 25°. At -80° the assumption seems valid.

The oxidized rhodium surface at -80° was found to be less susceptible to reduction. This result may support the possibility of the formation an intermediate product of the titration, *i.e.*, adsorbed hydroxyl groups. However, the above suppositions would not explain the experimentally observed initial decrease and further constancy of the titration results as the number of titration cycles increases. The number of hydroxyl groups and water molecules produced during one titration cycle would in fact be sufficient for evoking the effect.

Wanke and Dougharty<sup>5</sup> mentioned the analogous influence of the number of titration cycles on their results obtained under static conditions. They did not indicate, however, if their results reached a constant value. They suggested that the cumulative effect of water formation *in situ* on rhodium causing the decrease in titration results is due to the interaction between the water formed and hydrogen adsorption. The appreciation of the above suggestion is difficult. However, from Fig. 1 it follows that the introduction of water from outside into the system with the previously oxidized surface eliminates a further substantial decrease in the titration results. The situation seems to indicate that water formed *in situ* on the rhodium surface and the water from outside evoke practically identical final effects, *i.e.*, establishment of the results at a certain, almost identical, level. Thus the assumption about the blockage of part of the metal surface that is within the reach of the hydrated surface of a support seems to be justified. It would disprove, therefore, the above-mentioned<sup>5</sup> suggestion of the influence on hydrogen adsorption of water formed *in situ* on the metal surface. Our assumption indicates the equal dependence of both the hydrogen and oxygen adsorption on the water formed during the initial decrease in the titration results. The adsorptions would be limited only by the extent of participation of the metal surface not being subject to the action of the hydrated support.

The above assumption of the proportional decrease in the participation of oxygen and hydrogen adsorption in the total decrease in the titration results was indirectly tested in the following way.

After 14 successive cycles of titration with oxygen [ $(O_T)_{14} = 1.32$  (STP) cm<sup>3</sup> for a 4% Rh-Al<sub>2</sub>O<sub>3</sub> sample weighing 1.896 g] the temperature was increased to 500° and the remaining oxygen was titrated with hydrogen [ $H_T(500^\circ) = 2.08$  (STP) cm<sup>3</sup>]. This value corresponds to an oxygen adsorption value of  $(O_C)_{14} = 1.02$  (STP) cm<sup>3</sup>. The value [ $(O_T)_{14} - (O_C)_{14}] \cdot 2$  is equal to  $(H_C)_{13} = 0.60$  (STP) cm<sup>3</sup> and corresponds to hydrogen chemisorption in the thirteenth titration cycle. As the results of oxygen and hydrogen chemisorption on the "clean" surface of a sample were  $O_C = 1.67$  (STP) cm<sup>3</sup> and  $H_C = 1.05$  (STP) cm<sup>3</sup>, respectively, the decreases in the oxygen and hydrogen chemisorption values relative to the initial values were 39% and 43%, respectively. These values, in comparison with the decrease in titration results being about 44%, proves the proportionality of the influence of the decrease in titration results on those of both oxygen and hydrogen adsorption.

Platinum in titration reactions seems to behave in a different manner. As the number of the cycles increases a slight increase in results occurs<sup>3,6</sup>. However, one should not always seek an analogy between platinum and the other metals of the platinum group, taking into consideration, for instance, the differences in the reaction with oxygen at high temperatures.

In spite of this, a considerable decrease in hydrogen adsorption on platinum caused by the moisture present in the system has been reported<sup>7</sup>.

It seems that the decrease in titration results, which is disadvantageous in determining rhodium dispersion, can be applied in catalysis if water is present in the reaction system. Further investigations of the effect from the point of view of the influence of such factors as the degree of dispersion, distribution of the sizes of crystallites, pore structure of the support and measurement conditions seem desirable.

#### *Chemisorptive determination of rhodium dispersion*

The basic quantity necessary for the determination of metal surface areas by chemisorption methods is the stoichiometry of the adsorbate-metal surface interactions. As follows from Part I<sup>1</sup>, both hydrogen and oxygen chemisorption are very dependent on temperature.

With hydrogen the adsorption decreases with increase in temperature and with oxygen it increases within the range -80 to ca. 200°. The participation of the accompanying process, oxidation of the interior subsurface layers, decreases as the temperature decreases<sup>1</sup>. Therefore, the choice of any temperature for chemisorptive determinations of rhodium surface area has a smaller or greater uncertainty connected with the acceptance of a given stoichiometry of superficial interactions between rhodium and hydrogen (H/Rh<sub>s</sub>) or oxygen (O/Rh<sub>s</sub>) (where Rh<sub>s</sub> is a surface atom of rhodium). Metal dispersion can be determined by assigning values to H/Rh and O/Rh. Such a determination, however, is relative and is based on the assumption that H/Rh<sub>s</sub> and O/Rh<sub>s</sub> stoichiometries are constant and do not depend on the extent of metal dispersion. Table I gives the values of oxygen and hydrogen chemisorption (O/Rh and H/Rh) at ambient temperature. The values of the ratio of O/Rh to H/Rh range about from 1.3 to 1.7.

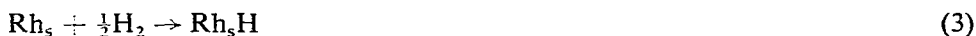
TABLE I

RESULTS OF OXYGEN AND HYDROGEN CHEMISORPTION AND OF HYDROGEN-OXYGEN TITRATION AT 25° FOR Rh-Al<sub>2</sub>O<sub>3</sub> CATALYSTS

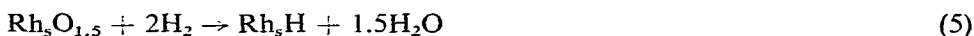
Catalyst		O/Rh	H/Rh	First titration with hydrogen: Rh <sub>s</sub> /Rh	First titration with oxygen: Rh <sub>s</sub> /Rh	O/Rh H/Rh	2/3 O/Rh - H/Rh H/Rh	(%)
Rh (%)	Condition							
4	Before sintering	0.31	0.20	0.21	0.21	1.55	+ 3.3	
4	2-h sintering in oxygen at 700°	0.25	0.18	—	0.16	1.39	- 7.2	
4	Oxidized and reduced many times within the range 500-700°	0.21	0.16	0.16	0.15	1.31	-12.5	
1	Before sintering	0.64	0.42	0.39	0.38	1.50	0.0	
1	Oxidation and reduc- tion many times at 670°	0.12	0.082	—	—	1.47	- 2.5	
0.5	Heated in oxygen at 400° for 2 h	0.42	0.25	—	0.28	1.68	+12	

\* Temperature of adsorption = -80°.

If we assume that the stoichiometry for rhodium is as suggested by Benson and Boudart<sup>8</sup> for the platinum-hydrogen system, *i.e.*, H/Rh<sub>s</sub> = 1 (which is generally accepted for not strongly dispersed catalysts), then a condition could be drawn that the stoichiometry of oxygen-rhodium interaction is O/Rh<sub>s</sub> = 1.5 with an accuracy of about ±15%. Hence the following simple equations can illustrate the reactions of oxygen and hydrogen chemisorption:



The reaction of hydrogen titration of the previously oxidized rhodium surface and the inverse reaction, *i.e.*, oxygen titration of the reduced surface, can be illustrated by the following equations:



From the above equations it follows that the ratio  $H_c:O_c:(H_T)_1:(O_T)_1$  would be 1:1.5:4:2, where  $H_c$  and  $O_c$  represent the chemisorption of hydrogen and oxygen, respectively, and  $(H_T)_1$  and  $(O_T)_1$  represent the amounts of hydrogen and oxygen used in the titration reactions 5 and 6. As the values decrease depending on the number of cycles, they refer only to the initial cycles. Based on reactions 5 and 6, rhodium dispersion was determined and the values are given in Table I. These results are in good agreement with the results of oxygen and hydrogen chemisorption. The last column in Table I gives relative differences between oxygen and hy-

drogen chemisorption calculated by means of the stoichiometry evident from eqns. 3 and 4. The differences lie within the range  $\pm 13\%$  of the average value. From the results in Table I it follows that the stoichiometry of the interaction between oxygen and rhodium ( $O/Rh_s = 1.5$ ) proposed by us is possible for a rhodium dispersion of  $D < 0.5$ . The value of the stoichiometry does not agree with that proposed by Bujanova *et al.*<sup>9</sup> (0.9). Wanke and Dougharty<sup>5</sup> found a value of  $O/Rh_s = 1.44$  for rhodium black at ambient temperature, taking into account the possible randomness of the value. It seems that at 25° our proposed value of  $O/Rh_s = 1.5$  can be justified if the assumed value of the stoichiometry ( $H/Rh_s = 1$ ) approximates to the real value.

The values of  $H/Rh > 1$  found by Wanke and Dougharty<sup>5</sup> reveal a clear validity for approximating the value to 1.5 when the dispersion increases to values close to 1.0. The values found by them suggest that the system of monoatomic dispersion of rhodium matches hydrogen with the stoichiometry  $H/Rh_s = 1.5$ . In our work we did not observe this result, probably owing to the low dispersions of the catalysts used ( $D < 0.5$ ).

Wanke and Dougharty<sup>5</sup> seem to think that within the temperature range 200–300° the stoichiometry of oxygen–rhodium interactions is *ca.* 1.5. Our investigations seem to contradict this conclusion. We relate the value of the stoichiometry  $O/Rh_s = 1.5$  rather to temperatures close to ambient, because at 200–300° bulk oxidation of rhodium occurs. The higher temperatures could be used for strongly dispersed systems for which the temperature of oxygen adsorption is not very important. We think, however, that under such conditions strongly dispersed rhodium catalysts could be subject to sintering.

It seems to us that both hydrogen and oxygen adsorption at low temperatures (0–100°) would be useful for the determination of the surface area of a dispersed rhodium metallic phase. Very low temperatures are not very convenient because both the hydrogen and oxygen stoichiometries change considerably in relation to temperature (0–100°) (Table I).

One should consider a number of factors that could influence both hydrogen and oxygen chemisorption. Oxygen, as an adsorbate in pulse gas chromatography, has the virtue of fast irreversible adsorption on the rhodium surface. Its main disadvantage is the possibility of adsorption on some subsurface oxide structures which are difficult to define quantitatively.

The basic disadvantage of hydrogen is the partly reversible character of its adsorption on the rhodium surface. In connection with the non-equilibrium conditions of pulse gas chromatography this feature may constitute a serious problem.

The contribution of hydrogen that could be removed with a stream of a carrier gas during a long period (15 h) is thought to be about 40%. Short times, say up to 2 h, would not result in removal of a contribution of reversible sorption of more than 10% of the total.

As follows from Table I, the initial cycles of titration would be suitable for the determination of rhodium dispersion. However, because of the necessity for removing moisture from the system, their practical usefulness for this purpose seems minimal.

Oxygen and hydrogen chemisorption give more explicit results although they require the pre-treatment of the catalyst and are not free from the above-mentioned problems.

The literature provides examples of the possibility of re-dispersion of the previously sintered metallic phase<sup>10</sup>. The practical importance of re-dispersion effects is very great. They allow a secondary activation of catalysts that have undergone sintering during the catalytic process.

The sintered rhodium–alumina catalysts that were used in multiple and sometimes very long processes of oxidation and reduction within the range 500–700° were subjected to tests of the re-dispersion effect. Oxidation was carried out at 670° under pulse conditions, then the catalysts were reduced by the pulse method at a given temperature and later underwent further reduction for 3 h in a stream of hydrogen. The catalysts were then washed with a stream of a carrier gas for 2 h and, after having been cooled to ambient temperature, underwent hydrogen chemisorption. The results of hydrogen chemisorption as a function of reduction temperature are presented in Fig. 3 (curves 1 and 2).

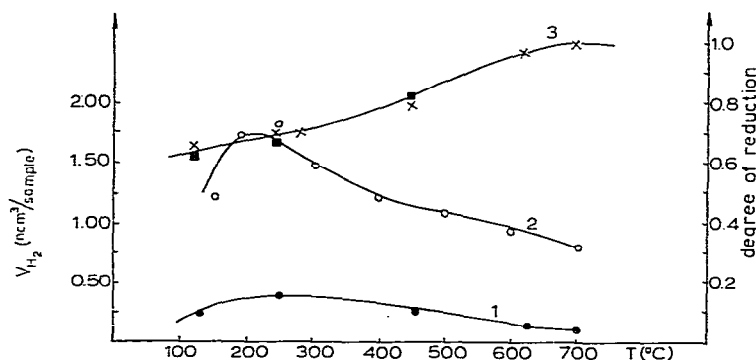


Fig. 3. Results of chemisorption and degree of reduction as a function of temperature. Catalyst: 1, 1% Rh-Al<sub>2</sub>O<sub>3</sub>; 2, 4% Rh-Al<sub>2</sub>O<sub>3</sub>; 3, 1% Rh-Al<sub>2</sub>O<sub>3</sub>. × = Pulse reduction; ■ = stream reduction (3 h). ● and ○ refer to the results of the curves 1 and 2, respectively.

An increase in reduction temperature first results in an increase in chemisorption, which reaches a maximum at about 280° and then decreases to values characteristic of 700°.

The course of the curves of hydrogen chemisorption seems to characterize the changes in the extent of rhodium dispersion, although their shape may be distorted for two reasons. Firstly, within the range 25–300° the results of hydrogen adsorption are lowered because of the expected considerable contributions of the adsorption that were not washed out with the carrier gas. Curves 1 and 2 should be situated higher as the temperature of reduction decreases. Secondly, there may be incomplete reduction of rhodium oxide within the range 25–500°. The extent of reduction for a 1% rhodium–alumina catalyst is illustrated by curve in Fig. 3. It was estimated from measurement of the amounts of hydrogen used during the initial stage of reduction with hydrogen pulses. It was tested by titrating the remaining oxygen with hydrogen at 700°.

Curve 3 may indicate that there is a strong interaction between the alumina support and the proportion of the rhodium oxide phase that is difficult to reduce.



This proportion is about 23–35% for temperatures up to 440°. An increase in temperature to *ca.* 500° results in almost complete reduction of rhodium oxide.

We consider that re-dispersion effects of rhodium catalysts are different from those characteristic of platinum<sup>10</sup>, because with rhodium it was the previously supported, completely oxidized rhodium in the form Rh<sub>2</sub>O<sub>3</sub> that underwent reduction and with platinum some strongly, but only superficially, oxidized platinum metallic catalysts were subject to reduction. An alternative interpretation of curves 1 and 2 in Fig. 3 could be a spillover process of hydrogen from metal on to the support, made easier because of the presence of a partial rhodium oxide phase and larger (in relation to the situation at 500°) amounts of water in the system<sup>11</sup>.

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