

Induction of Catalytic Activity of Rhodium in Ethylene Hydrogenation by the H₂-O₂ Reaction

ANNIE AMARIGLIO AND HENRI AMARIGLIO

Laboratoire Maurice Letort (C.N.R.S.), Route de Vandoeuvre, Boîte Postale No. 104, 54600 Villers-Nancy, France and Université de Nancy I, Boulevard des Aiguillettes, 54037 Nancy Cédex, France

Received April 18, 1979; revised May 19, 1980

Rh ribbons have been used as catalysts for C₂H₄ hydrogenation at atmospheric pressure and for temperatures ranging from about 100 up to 300°C. The catalytic activity is shown to be heavily dependent on various oxidation-reduction treatments and on the presence of O₂ traces in the reactant mixture. Different experiments show that this behavior cannot be understood as the result either of contaminations and cleaning of the surface or of a modification of surface properties by chemisorbed O₂. The best explanation is that of a structural sensitivity of the metal surface to the H₂-O₂ reaction through the surface mobility it induces. The content of active sites is determined according to the rate of their chemical generation and that of their disappearance by thermal restructuring of the surface. Many kinetic features of the system (and especially transient behavior) are thereby accounted for and proof of significant rearrangements of the surface is obtained by optical and electron microscopy.

INTRODUCTION

We have already reported on the large promoting influence of O₂ traces upon the catalytic activity of different metals in the hydrogenation of C₂H₄ (1-4) between about 100 and 300°C. We have proposed explaining this influence by the generation of lattice disturbances which might behave as efficient active centers on the metal surfaces. These disturbances have to be conceived as surface defects with a limited lifetime since the dislodged atoms tend to find more stable positions. The effects of various pretreatments of the catalysts could also be accounted for according to their ability to allow O₂ to accumulate on the surface or to maintain the latter in a reduced state and to let it anneal under a reducing atmosphere. Various important kinetic characteristics of these catalysts (and especially the occurrence of a maximum in activity versus temperature) have been interpreted in relation with this effect (1-4) and proof of the induced atomic mobility of the metal has been given (5) by making gross surface rearrangements ap-

pear under the influence of reacting conditions.

Since our first work, new information has become available about the positive influence that O₂ may exert on hydrogenation reactions catalyzed by metals (6-11). Moreover, this action is no longer necessarily conceived of as resulting from a cleaning of the surface. In order to understand this important effect more thoroughly and to know whether it can occur on other transition metals, we have examined Rh especially as it is known to be the best catalyst for this reaction (12-14).

EXPERIMENTAL

Kinetic measurements. The kinetic experiments have been performed in a flow-type apparatus at atmospheric pressure.

The main gases which have been used throughout this work are He, H₂, and C₂H₄. In order to have them carefully purified, the gases pass through successive purifiers: Ni and Pt dispersed on SiO₂ (25°C; O₂ in H₂), CuO (250°C; H₂ and CO in He or C₂H₄), nonstoichiometric manganese oxide (25°C; O₂ in C₂H₄ or He), Ag (25°C; sulfur com-

pounds in C₂H₄), a trap filled with glass beads at dry ice temperature for C₂H₄ or with molecular sieve at liquid air temperature for He or H₂. Except for the reactor, the whole apparatus is made of stainless-steel pipes with Swagelock fittings and metallic 4-port or 6-port valves. The flows of gases are maintained constant by Brooks flow-controllers. The mixture H₂-C₂H₄ is always 5% C₂H₄, 95% H₂.

The reactor is made of a quartz U-tube (i.d. = 4 mm). The catalyst ribbon is placed in the bottom of the reactor and along its axis. Using a 4-port switching valve, the reactor may be fed with the reactant mixture (or any other gas) or merely closed. A 6-port sampling valve, which is set ahead of the reactor and its switching valve, allows the sending of minute doses of air or oxygen into the reactant mixture.

After purification, all the gases may be enriched with oxygen (from a few ppm to 100 ppm) as they flow inside a Teflon permeation tube which is maintained at a fixed temperature under a constant pressure of air or oxygen. The precise oxygen content of every gas is measured by means of an oxygen-meter (Engelhard Mark II electrochemical meter); the most sensitive range of this meter (0-10 ppm) allows a correct measurement of 1/10 ppm. The flow-rate through this analyzer has an imposed value of 133 cm³/min and for this reason the rate measurements have been made at this flow-rate value.

The extent of reaction is known from a chromatographic analysis (Intersmat IGC 12 F, using F.I.D.; 13X molecular sieve column, 210°C).

Auger spectroscopy. Auger analyses have been used to obtain the composition changes which may affect the surface during the transient states in order to look for some parallelism between them and the rate changes. The experimental arrangement consists of a Leybold-Heraeus spectrometer equipped with a preparation chamber which may be fed with gases at atmospheric pressure. The sample may be quickly trans-

ferred from it into the analysis chamber while being maintained under vacuum.

Optical and scanning microscopes. The rearrangement of the surface induced by the H₂-O₂ reaction has been observed with the help of an optical microscope (Leitz; Panphot type), using an experimental arrangement previously described (5) and allowing observation of the sample during the reaction. When sufficient surface modifications had been detected, they were examined with a scanning electron microscope (Cameca MEB 07; sample at an angle of 28° with the horizontal).

Catalysts. The samples used in this work are pieces of a rhodium ribbon (Heraeus; 99.99% purity), 3/100 mm thick, 1 mm wide, and 2 cm long (0.2 cm² geometric area). They are cleaned with distilled water, alcohol, and acetone before being introduced into the reactor.

RESULTS

1. First Run

Usually the first run consists in observing the rate of ethane production when the catalyst is flushed with the carefully purified reactant mixture and the temperature of the metal is increased according to a constant rate of 6 or 8°C/min.

Figure 1, curve I or I', shows that a drastic rise of activity appears at about 200°C and is followed by a fast decrease which results from a catalyst deactivation adding to the usual occurrence of a maximum activity against temperature. When the highest temperature has been reached it is maintained for some time which allows one to observe a decreasing activity. The temperature is then decreased in the same regular fashion (curve II). The mean activity level is then much lower. Curve III is obtained for immediately reincreasing temperatures.

The catalyst is then flushed with pure H₂ at 400°C overnight. This operation is repeated before any of the reactivating treatments which will be described in the next

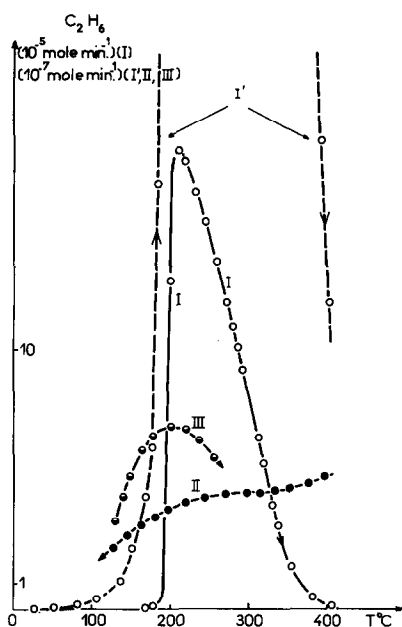


FIG. 1. First run of C_2H_4 hydrogenation: variation of the rate of reaction as a function of temperature. Reactant mixture: 95% H_2 , 5% H_2 , O_2 content < 0.1 ppm. Rate of temperature increase (I or I', III) or decrease (II): $6^\circ C \text{ min}^{-1}$.

section. It results in a strong deactivation which would be reinforced if the exposure to pure H_2 was prolonged. The deactivation can be made observable by returning to some reference conditions. Typically, at $200^\circ C$, rates lower than $10^{-7} \text{ mole min}^{-1}$ can be measured and that constitutes a reference for estimating the extent of a further reactivation as will be referred to in the next section.

2. Application of Various Pretreatments

2a. Mild oxygen treatments. The mildest way of submitting the metal to oxygen in a reactor working at atmospheric pressure is to dilute this gas by an inert carrier gas. Therefore the rhodium sample is flushed with helium, carefully purified, and typically enriched with an oxygen content of about 20 ppm. The exposure is continued for several hours and frequently at about 250 or $300^\circ C$. However, lower tempera-

tures have been applied ($100^\circ C$), the resulting effect being qualitatively the same.

Following the $He-O_2$ pretreatment, the reactant mixture is directed toward the catalyst, maintained at the same temperature. In every case an activation results and is followed by a deactivation which may present complex features that we shall report later. Figure 2 shows the simplest case of a regularly decreasing activity.

Another manner of illustrating the action of an $He-O_2$ mixture is to decrease the catalyst temperature after the exposure and to plot the catalytic activity against temperature when the latter is reincreased linearly with time. At the same time the O_2 content of the exit gas is continuously recorded. Figure 3 shows the result of this kind of experiment and it is worth observing that the optimum hydrogenation activity occurs at a temperature for which an optimum rate of the oxygen consumption also occurs.

2b. Severe oxygen treatments. A more direct way of exposing the metal to oxygen is to flush it with purified air. Figure 4 shows the catalyst behavior at $300^\circ C$ following such pretreatments. The reproduc-

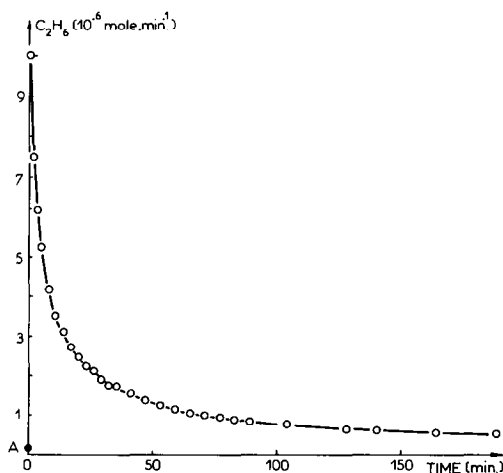


FIG. 2. Variation of the rate of C_2H_4 hydrogenation at $158^\circ C$ as a function of time after reactivation by an $He-O_2$ pretreatment at the same temperature. The activity before pretreatment is given by point A. Pretreatment: 3 min in a flow of pure He ; 52 min in a flow of $He-30 \text{ ppm } O_2$; 3 min in a flow of pure He . Reactant mixture: 95% H_2 , 5% C_2H_4 , 0.8 ppm O_2 .

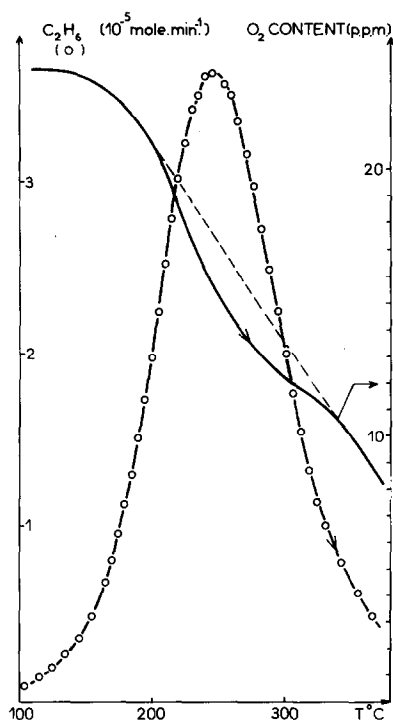


FIG. 3. Simultaneous variations of the rate of C₂H₄ hydrogenation and of the O₂ content of the exit gas as a function of temperature after an He-O₂ pretreatment. Pretreatment: 3 min in a flow of pure He; 25°C; an increase of temperature up to 250°C in the same gas; 2 hr in a flow of He-24 ppm O₂; 250°C; a decrease of temperature down to 100°C in the same mixture; 3 min in pure He; 100°C. Reactant mixture: 95% H₂, 5% C₂H₄, 24 ppm O₂. Rate of temperature increase: 4°C min⁻¹.

ibility of the activating action appears quite good. Comparison of curves 1 and 2 shows that the deactivation takes place in about the same manner under the flush of reactant mixture or when the reactor is by-passed and the catalyst confined in the reactant mixture. In a related way a large part of the activating action disappears if the oxygen pretreatment is followed by an H₂ exposure before measuring the catalytic activity (curve 3). The deactivation takes place in about the same manner under H₂ or under the reactant mixture. Curve 4 is obtained after a long deactivation (15 hr in a flow of reactant mixture; activity reduced nearly 13 times). The deactivation proceeds more rapidly along curve 5 due to the lower O₂

content of the reactant mixture. The attainment of the steady rate would require more than 1 day and its value depends on the O₂ content of the reactant mixture.

At lower temperatures similar curves can be obtained. However, as the reduction of the initially preoxidized surface by the reactant mixture is slower, the usual deactivation may be preceded by a short period of rate increase.

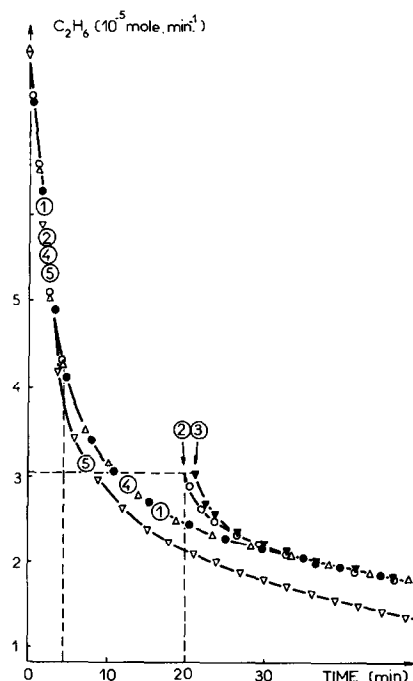


FIG. 4. Variation of the rate of C₂H₄ hydrogenation at 300°C as a function of time after activation by air under various conditions. Activity before the first pretreatment: $\approx 10^{-6}$ mole min⁻¹. Pretreatments: ● curve 1: 15 hr in a flow of air; 350°C; ○ curve 2: 15 min in a flow of air; 300°C; (between times 4 min 30 sec and 20 min the reactor is by-passed and the catalyst confined in the reactant mixture); ▼ curve 3: 15 min in a flow of air; 300°C; 21 min in a flow of (H₂-4.7 ppm O₂); 300°C; △ curve 4: 1 hr in a flow of air; 300°C; ▽ curve 5: 15 min in a flow of air; 300°C. Curves are numbered consecutively in the order in which they were obtained; only curve 3 has been continued for 15 hr (rate reached: $7 \cdot 10^{-6}$ mole min⁻¹) before undertaking the activating pretreatment related to curve 4. For the other curves the catalyst has been exposed to the flow of reactant mixture for about 50 min. Reactant mixture: 95% H₂, 5% C₂H₄, 4.7 ppm O₂ (curves 1, 2, 3, and 4); 95% H₂, 5% C₂H₄, 0.7 ppm O₂ (curve 5).

As for the case of He-O₂ mixtures, another way of showing the action of an air pretreatment is to bring the sample back to room temperature and then to follow its activity against temperature when the latter increases linearly. Once the temperature has reached its highest value, it can then be linearly decreased, allowing one to obtain curves relating to decreasing temperatures as well. Figure 5 shows how increasing the severity of the O₂ treatment results in

stronger effects in C₂H₄ hydrogenation and H₂-O₂ reaction as well. The transient extraactivity originating from a severe O₂ treatment causes the rate of O₂ consumption to be abnormally high at low temperatures (depressed part of curves A and B). The strength of activation can also be evidenced by the lowering of the temperature at which some reference rate is reached in the course of the same program of increasing temperature.

Pretreatment by an air flush	15 hr; 250°C	15 hr; 350°C	48 hr; 400°C
Temperature at which a rate of 10 ⁻⁴ mole min ⁻¹ is reached for C ₂ H ₄ hydrogenation	200°C (Fig. 5; curve 1)	110°C (Fig. 5; curve 2)	90°C (without O ₂ in the reactant mixture)

Figure 6 relates to the case of the H₂-O₂ reaction occurring alone. The activating influence of the O₂ pretreatment is evidenced by the same depression as in curves A and B of Fig. 5.

3. Introduction of Small Oxygen Doses to the Reactant Mixture

A very easy way of illustrating the promoting influence of O₂ is to introduce a small amount of O₂ or air into the reactant mixture by the rapid rotation of a 6-port sampling valve whose loop is permanently flushed with air. The activation follows immediately if the temperature is high enough. Figure 7, relating to 250°C, shows that this operation can be repeated resulting in a regular increase of activation. The latter levels off at a high value, more rapidly attained at higher temperatures.

4. Steady Activity versus Oxygen Content

The O₂ effect has been shown in transient modes by the preceding experiments and this makes it obvious that the O₂ content of the reactant mixture should be an important factor of the catalytic activity in the steady

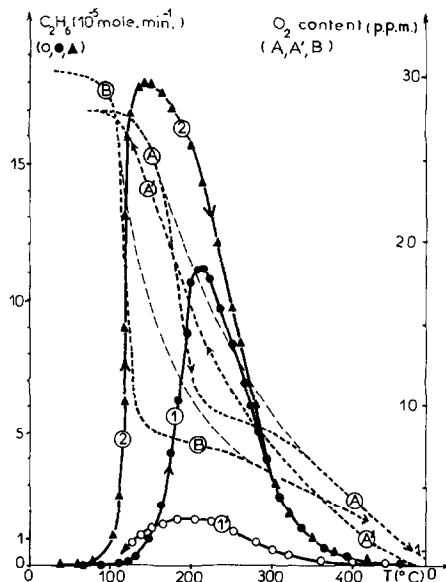


Fig. 5. Simultaneous variations of the rate of C₂H₄ hydrogenation and of the O₂ content of the exit gas as a function of temperature after two different air pretreatments. Pretreatments: 1: 15 hr in a flow of air; 250°C (curves 1 and A); curves 1' and A' are obtained immediately after 1 and A; 2: 15 hr in a flow of air; 350°C (curves 2 and B). Reactant mixture: 95% H₂, 5% C₂H₄, 28 ppm O₂ (A, A', 1, 1'); 95% H₂, 5% C₂H₄, 30 ppm O₂ (B, 2). Rate of temperature increase (curves 1, 2, A, B) or decrease (curves 1', A'): 6°C min⁻¹.

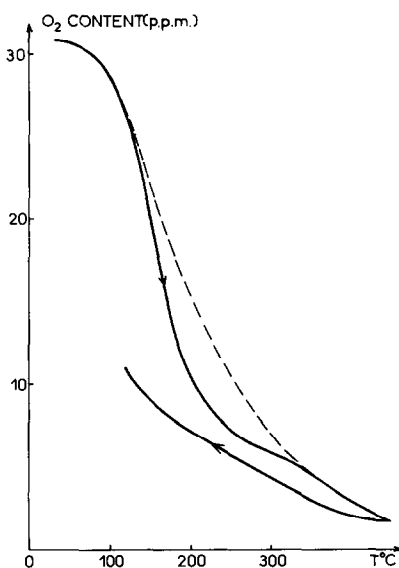


FIG. 6. Variation of the O₂ content of an H₂-O₂ mixture as a function of temperature. Pretreatment: 15 hr in a flow of air; 250°C. Reactant mixture: H₂ + 31 ppm O₂. Rate of temperature increase: 6°C min⁻¹.

state. However, obtaining the steady activities of the sample against temperature and for different O₂ contents of the gas is a very difficult task due to the length of the transient responses of the catalyst whenever a kinetic factor, such as temperature or O₂ content, is varied. The description of such behavior will be given in the next section. What matters now is that the slowness of the catalyst responses entails that several weeks are needed to establish curves such as those of Fig. 13. Moreover, attainment of the true stationary state is somewhat questionable since the crystallographic state of the surface is continuously modified throughout the entire time of reaction, as will be shown later. As this surface rearrangement proceeds faster when the rate of the H₂-O₂ reaction is higher, "steady" activities have been measured through decreasing temperatures or decreasing O₂ contents. Activities were considered as stationary when they varied less than 3-5% per day. If this test of the stationary condition had been changed somewhat different curves would have

been obtained. Thus the activities reported in Fig. 8 must be considered as relating to some definite procedure and to a certain state of the sample evolution as well. They could not have been exactly reproduced even with the same sample and the same procedure some weeks later.

5. Transient Responses of the Catalyst to a Change of Temperature or Oxygen Content

As previously stated, any sudden change in any kinetic parameter results in a transient response of the catalyst. We shall report in a later article on the most meaningful catalyst behavior determined by a change in ethylene content. All of the experiments carried out in this work have been performed with the same C₂H₄/H₂ ratio and only the transients following a change of temperature or of oxygen content have been considered.

5a. Change of temperature. The most interesting transient responses occur in the neighborhood ($\pm 40^\circ\text{C}$) of the temperature giving the maximum activity, T_{max} . In this temperature range and for a small change of temperature, there are two steps in the rhodium response. The first step is fast and

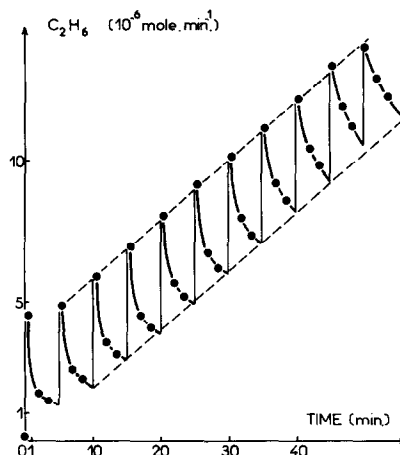


FIG. 7. Successive activations and deactivations obtained at 250°C by introducing small doses of O₂ into the reactant mixture. O₂ dose: ≈ 0.1 ml. Reactant mixture: 95% H₂, 5% C₂H₄, 0.7 ppm O₂.

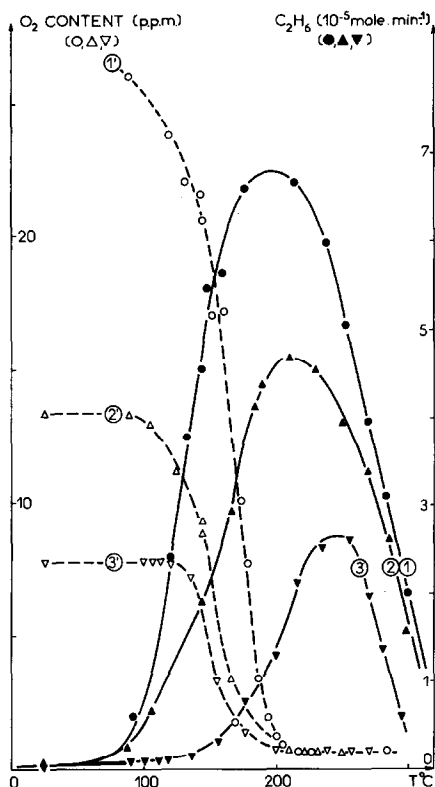


FIG. 8. Simultaneous variations of the steady rate of C_2H_4 hydrogenation and of the steady O_2 content of the exit gas as a function of temperature, for various O_2 contents of the reactant mixture. Reactant mixture: 95% H_2 , 5% C_2H_4 , 30.5 ppm O_2 (curves 1 and 1'); 95% H_2 , 5% C_2H_4 , 13.4 ppm O_2 (curves 2 and 2'); 95% H_2 , 5% C_2H_4 , 7.8 ppm O_2 (curves 3 and 3').

always in the direction expected from the Arrhenius law. However, soon afterwards, a slow change starts in the opposite sense and progressively leads the catalyst to its new steady state which is higher or lower than the initial one according to the precise location of the final temperature with regard both to the initial one and to T_{max} .

5b. Change of oxygen content. Basically the catalytic activity increases with the oxygen content of the gas but the precise path of the rate variation following a change of oxygen pressure depends on temperature. At a high enough temperature, the rate varies directly with the oxygen content. However, at lower temperatures the activating oxygen influence combines with

the well-known inhibition effect due to site coverage. Figure 9 shows what occurs at $172^\circ C$ when the oxygen content first increases from 0.35 to 23 ppm and then decreases to its initial value. It is worth noting that the inhibition effect appears or disappears at once whereas the promoting action needs a long period in order to establish itself at its steady value or to disappear completely.

6. Preliminary Conclusions

It follows from the whole set of experiments which have just been described that oxygen is able to exert a high promoting influence upon the course of ethylene hydrogenation but more experimental investigation is needed before the true nature of this action can be asserted. Nevertheless, we can already notice that the length of the deactivation periods shows that it is likely that O_2 still exerts its effect after most of the preadsorbed oxygen has been extracted from the surface. Moreover, the possibility of explaining the O_2 influence by a cleaning effect as was suggested in the case of Pt (15, 16) is not very convincing with respect

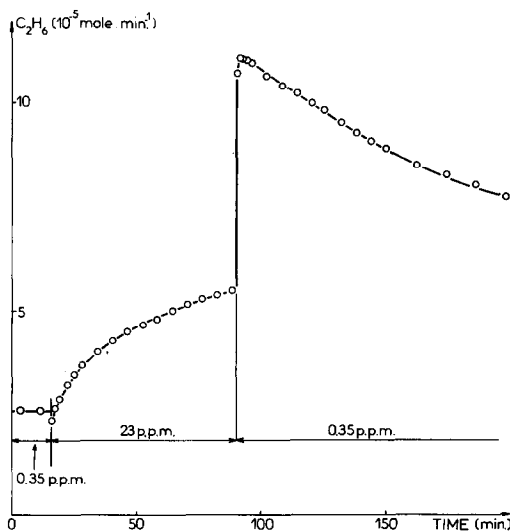


FIG. 9. Variation of the rate of C_2H_4 hydrogenation as a function of time, at $172^\circ C$, when the O_2 content of the reactant mixture varies from 0.35 to 23 ppm and inversely. Reactant mixture: 95% H_2 , 5% C_2H_4 .

to the deactivation observed during the exposure of rhodium to pure H₂. However, these two points deserve more direct experimental evidence especially if one takes into account the possible segregation of impurities on the metal surface which may be induced by H₂ chemisorption itself (17, 18). Thus, we were led to undertake Auger analyses of the surface after various pretreatments.

7. Surface Analysis

The overall conclusions of such experiments will be published elsewhere. Here, we will only summarize some of the main points.

The rhodium used is initially contaminated by C, S, Ca, and P. When it is flushed by H₂ at 300°C and at atmospheric pressure, it progressively purifies itself of S, P, and Ca. Thus the deactivation observed after a long pretreatment by H₂ in the same conditions cannot be assigned to an induced segregation of S, for example. C is easily removed by O₂, more slowly and less completely by H₂. Finally a sequence of six to ten treatments first oxidizing and then reducing at 400°C and at atmospheric pressure makes it possible to clean the sample properly (Fig. 10). The spectra thus obtained compare well with the spectra obtained by other authors (7, 19, 20). Heating the clean sample once again at the same temperature, under vacuum or under a flow of H₂, does not lead to the detection of any further increase of contaminant.

The exposure of the sample to the reactant mixture causes a quick though limited increase of C which soon becomes constant (between 5 and 10 min) (Fig. 11). The O₂ content stays constant as well so that the changes of the surface composition with regard to these two components cannot explain the transient state during the exposure of Rh to the reactant mixture after an O₂ pretreatment (cf. Fig. 4).

It follows from these analyses that there is no parallelism between changes of the

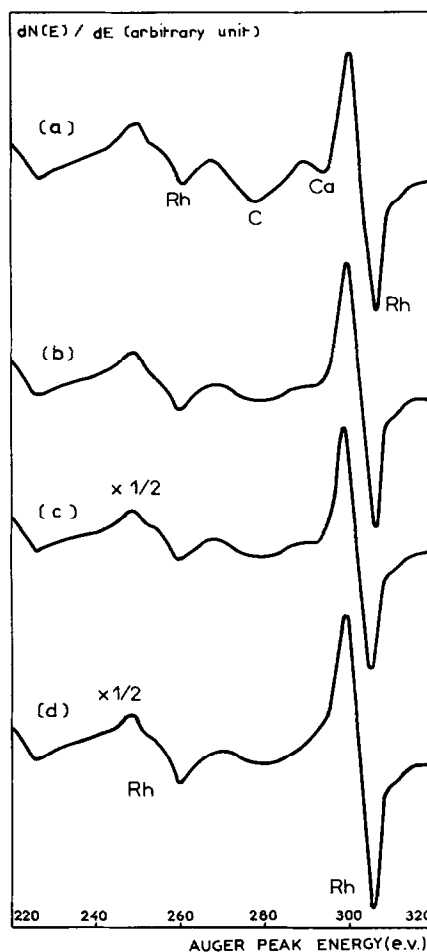


FIG. 10. Auger electron spectra of a Rh ribbon after cleaning treatments. (a) Spectrum of the ribbon successively cleaned by different solvents (H₂O; C₂H₅OH; CH₃-CO-CH₃; C₂H₅OH; H₂O; C₂H₅OH); and after a H₂ treatment (2 hr 15 min; 400°C; atm. pressure); (b) after 1 sequence O₂ (15 min; 400°C; atm. pressure), H₂ (15 min; 400°C; atm. pressure); and 5 sequences O₂ (5 min; 400°C; atm. pressure), H₂ (5 min; 400°C; atm. pressure); (c) after a supplementary H₂ treatment (40 min; 400°C; atm. pressure); (d) after an Ar⁺ bombardment ($\approx 1 \mu\text{A}$; 15 min; 400°C).

surface composition and the transient catalytic activities of rhodium.

8. Kinetic Search for the True Cause of Activation

The use of physical means shows that the catalytic behavior during transient states does not parallel changes in the chemical

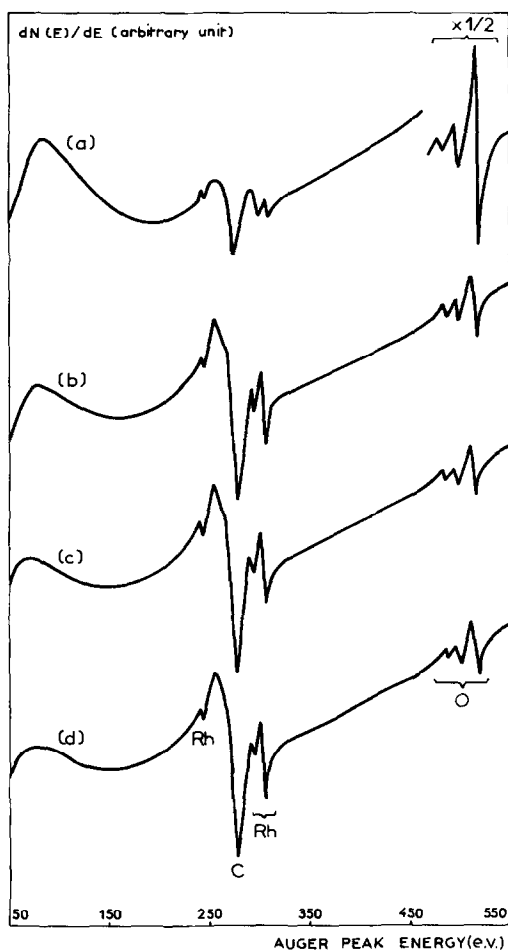


FIG. 11. Auger electron spectra of a Rh ribbon after exposures of various lengths to the reactant mixture (97.5% H_2 ; 2.5% C_2H_4 ; 300°C; atm. pressure). (a) Before any exposure and after an activating pretreatment (O_2 ; 15 min; 400°C; atm. pressure); (b) after an exposure of 5 min; (c) after an exposure of 10 min; (d) after an exposure of 26 min.

composition of the whole surface. Nevertheless, these physical means come up against the objection that no sure conclusion should be made if it happens that the sites responsible for the catalytic activity are so few that the species they comprise do not appreciably contribute to the composition detected by the Auger analysis.

Thus we revert to new kinetic experiments able to distinguish between chemical effects of oxygen and structural ones. Any explanation of the oxygen effect based

upon its decontaminating efficiency or the promoting influence that its presence on (or near) the surface might exert assumes that this effect is a property of O_2 only. On the contrary, explaining the oxygen effect by the structural sensitivity of the surface to the H_2 - O_2 reaction amounts to thinking that the true activating agent is not to be found in O_2 alone but in the chemical events which happen during the fixation of O_2 on the surface and its subsequent extraction by H_2 .

The two kinds of experiment which will now be reported have been undertaken in order to decide which of these two types of interpretation fits better. For this purpose, the exposures to O_2 and H_2 have been carried out successively rather than simultaneously as before. Furthermore, great care has been taken to prevent mixing of H_2 and O_2 when substituting one gas for another one (intermediate flush of helium). Both kind of experiments have been undertaken at about 200°C where transient phenomena proceed at a medium rate.

8a. Comparison between the actions of He- O_2 and H_2 - O_2 mixtures at a moderate temperature. In these experiments, once pretreated, the catalyst is maintained at the experiment temperature (205°C) under a flow of H_2 or ($H_2 + O_2$), according to the experiment, and its activity in C_2H_4 hydrogenation is measured by periodically feeding the reactor with the reactant mixture (deprived or not from O_2 , according to the experiment), for 30 sec only. This reduces the possible hydrocarbon contamination of the surface to the best feasible extent.

First of all, the catalyst is deactivated by a long H_2 exposure at about 300°C. It is then cooled to the temperature of the experiment and its residual activity is measured by feeding the reactor with the reactant mixture without O_2 for 30 sec only. An He- O_2 mixture is now directed toward the metal for several hours after which the reactant mixture (with the same O_2 content) feeds the reactor for 30 sec only, to measure the initial gain of activity. The latter

turns out to be the same after a pretreatment of 2 or 22 hr (point A; Fig. 12) and so reveals some kind of limitation in the action of the He-O₂ mixture. The rhodium sample is now flushed with an H₂-O₂ mixture with the same oxygen content and the catalytic activity is measured about every 15 minutes. Curve 1 of Fig. 12 shows the most remarkable behavior of the so pretreated rhodium.

In another experiment, after the preliminary deactivation under pure H₂ at 300°C, the catalyst is directly flushed with the H₂-O₂ mixture and the kinetic determinations are carried out in the same periodic way. Curve 2 of Fig. 12 gives the result of such a procedure.

Two points are worth being stressed. First the same final steady state is eventually reached but in quite different ways. Moreover, we can notice that the activity

level reached after having flushed the catalyst with the H₂-O₂ mixture for 15 min (point B) is higher than the level reached after having flushed it for 22 hr by the He-O₂ mixture (point A). Obviously this single result rules out the possibility of attributing the activation effect to oxygen only.

Nevertheless, comparison of curves 1 and 2 might suggest that some optimum oxygen coverage would be transiently obtained and so might explain the maximum in curve 1, for a surface having first been completely covered with O₂ and progressively uncovering itself in a flow of (H₂-O₂). However, in order that such an assumption could hold, the coverage changes should be very slow and this seems to be excluded due to the order of magnitude of the rate usually observed for the H₂-O₂ reaction. Besides, the incorrectness of this view can be proved by another experiment

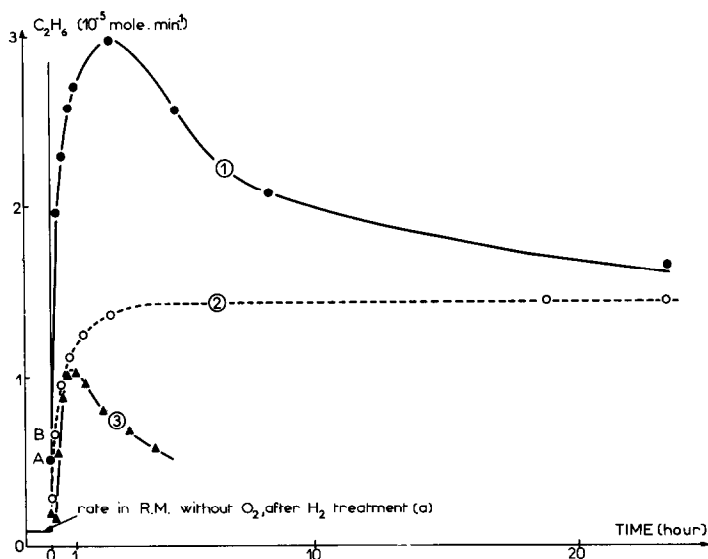


FIG. 12. Variation of the rate of C₂H₄ hydrogenation at 205°C as a function of time, after He-O₂ or H₂-O₂ pretreatments. Curve 1. Pretreatments: (a) 15 hr in a flow of pure H₂; 300°C; decrease of temperature down to 205°C in a flow of H₂; (b) 3 min in a flow of pure H₂; 205°C; (c) 22 hr in a flow of (He-18 ppm O₂); 205°C; (d) 3 min in a flow of pure He; 205°C. Measurement: The catalyst is then maintained in a flow of (H₂-18 ppm O₂) and its activity is monitored by flushing it with the reactant mixture (95% H₂; 5% C₂H₄; 18 ppm O₂) for 30 sec and about every 15 min. Curve 2. Pretreatments (a) and (b) are directly followed by the kinetic measurements under the same conditions. Curve 3. Pretreatments (a), (b), (c') 19 hr 30 min in a flow of (He-18 ppm O₂); 205°C; (d). Measurement: The procedure is the same as for curves 1 and 2 but H₂ and the reactant mixture (95% H₂; 5% C₂H₄) are free from O₂.

which leads to curve 3 (Fig. 12). Following the same He-O₂ exposure as that giving rise to curve 1, the rhodium is flushed with pure H₂ and kinetic measurements are performed as previously but using a reactant mixture *without* O₂. If the increasing part of curve 1 was explained by a progressive reduction of the surface, this reduction should be faster now and higher activities should be displayed. Just the contrary is observed, since the absence of oxygen in the gas during this period makes the reactivity lower. No oxygen excess on the surface can therefore account for the upper curve maximum. We shall propose an explanation of that in the Discussion.

8b. Effect of successive oxidizing and reducing exposures. Another way of discriminating between an effect due to oxygen only and that of oxidation-reduction cycles consists in subjecting the metal to alternate oxygen and hydrogen exposures and measuring any progress in activation between two successive cycles.

To this end, the rhodium sample is first deactivated (15 hr, H₂, 300°C). After cooling at 198°C, the remaining activity is measured by a 30 sec flush of reactant mixture deprived of O₂. The metal is then exposed to an He-O₂ mixture at the same temperature for 80 min. A small activation results, as is shown by a new 30 sec flush of reactant mixture. From this time onward, the He-O₂ exposures are reduced to 5 min whereas the activity probes are performed by 30 sec flushes of deoxygenated reactant mixture. In order to avoid any diffusion of H₂ into O₂ (and reciprocally) and the effect of the H₂-O₂ synthesis, the flows of He-O₂ and H₂-C₂H₄ are separated by a feed of pure He for 2 min (each cycle lasts 9 min 30 sec). Every short flush of the reactant mixture constitutes a brief reducing exposure and allows following the activation progress at the same time.

The result of the experiment is shown in Fig. 13. Clearly each oxidation-reduction cycle entails a new step in the catalyst activation. What is still obvious is that the

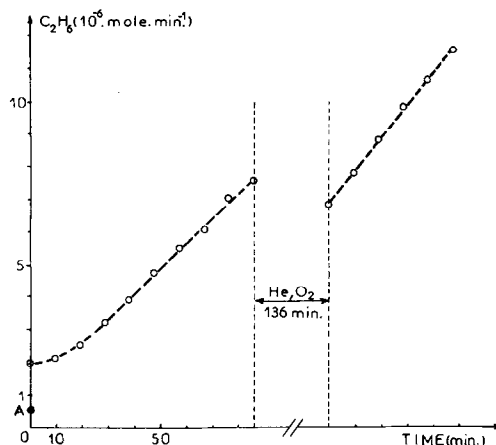


FIG. 13. Activation by alternately oxidizing and reducing exposures at 198°C. Pretreatment: 15 hr in a flow of pure H₂; 311°C; decrease of temperature down to 198°C; 80 min in a flow of He-14 ppm O₂. Each cycle lasts 9 min 30 sec and comprises a succession of flushes by (He-14 ppm O₂) (5 min), He (2 min), (95% H₂, 5% C₂H₄) (30 sec), He (2 min). The activity before pretreatment is given by point A.

activation is faster when O₂ and H₂ are sent alternately during a given time than when the catalyst is exposed to only O₂ for the same time. Most meaningful with regard to this statement is the stop in activation which results from the interruption of the cycles and a long exposure to He-O₂ only, whereas the activation continues, and at the same speed, as soon as the composite treatment is taken again.

Therefore the true cause of activation turns out to lie in the O₂ binding to the surface added to the further action of H₂. If one now takes into account the ability of Rh surfaces (like other metal surfaces) to reconstruct under O₂ exposure (20, 21), the assumption of lattice distortions which should occur when H₂ removes O₂ from the surface appears reasonable. If this view is accepted, active centers are expected to be constituted (partially at least) of dislodged atoms and (or) lattice vacancies. An intrinsic cause of catalyst deactivation would then be the irreducible tendency of the surface to restructure. However, the final positions of the dislodged atoms should have a fair chance of differing from their

initial ones. The H₂-O₂ reaction would then speed up the self-diffusion of surface (and near surface) atoms in order to allow the appearance of a surface configuration of the metal better fitting the conditions to which the latter is subjected.

9. *Rearrangement of the Surface Induced by the H₂-O₂ Reaction*

It has already been abundantly demonstrated that a metal surface can undergo very gross modifications during the course of the H₂-O₂ reaction (23-25) or under electrochemical oxidation-reduction treatment even at room temperature (26). We have already shown (5) that facetting can occur on Ni and Pt at low temperatures and for O₂ contents much smaller than those usually employed.

We report in Fig. 14 similar results obtained in a similar manner with rhodium. The first sample was initially thermally smoothed by heating it at 1480°C for 12 hr under pure H₂. Micrographs 1 to 3 show the effect resulting from a feed with H₂-2000 ppm O₂ for 5 days at 250°C and then 14 days at 330°C. The second sample was mechanically polished and then cleaned before being fixed in the experimental set-up. Micrographs 4 and 5 show the effect resulting from a feed with H₂-2000 ppm O₂ for 21 days at 450°C.

Care has naturally been taken to show that no rearrangement occurs during similar times when the metal is exposed to pure H₂ or to an He-O₂ mixture with the same O₂ content as in the reactant mixture and at the same temperature.

The pattern of small facets which develops on the rhodium surface is very dense and does not appear at the same rate on the various grains of the metal. Some parts of the surface remain unaffected, most probably because of their orientation.

Micrograph 6 in Fig. 14 is interesting in that it shows the profound modifications which resulted on a Rh sample in the course of 5 months of various kinetic experiments. The oxidation-reduction treatments to

which it had been submitted were especially numerous and most of them were applied in the range of 200-400°C. Obviously massive surface diffusion was induced during the course of reaction. The crackled aspect of the surface compares well with that of some Pt-Rh gauzes used in the industrial oxidation of NH₃ (27) and leads one to thinking that quite random orientations may result in the long run.

We therefore arrive at the same conclusion as before concerning the mobility of the surface which is undeniably induced by the H₂-O₂ reaction.

DISCUSSION

The promoting influence of O₂ has already been recognized by other authors in cases of this gas being used as a pretreating agent. In addition we have shown that it may exert its action continuously when it is contained in the reactant mixture as an impurity. Some authors (15, 16) have proposed that its action results from a cleaning effect, whereas others (6-10, 28) have argued that traces of oxygen are able to stay long enough on surfaces or in subsurface regions, even under the reducing mixture, and to induce some modification of the surface properties in a positive way.

There are numerous experiments in the present work which make it possible to discard the explanation of the oxygen effect as the mere result of a decontamination. Had the contaminant been ethylene, no progress in the deactivation could have been observed under pure H₂. The latter cannot be reasonably identified with a contaminant carrier, because of the drastic purification to which it has been submitted. Moreover, the deactivation under H₂ is the same no matter what the origin and purification of the gas may be (commercial gas bottle or electrolytic preparation; usual purification or diffusion through a palladium thimble).

However, the possibility that the surface might have been contaminated by some impurity segregating from the bulk must not be overlooked, especially with reference to

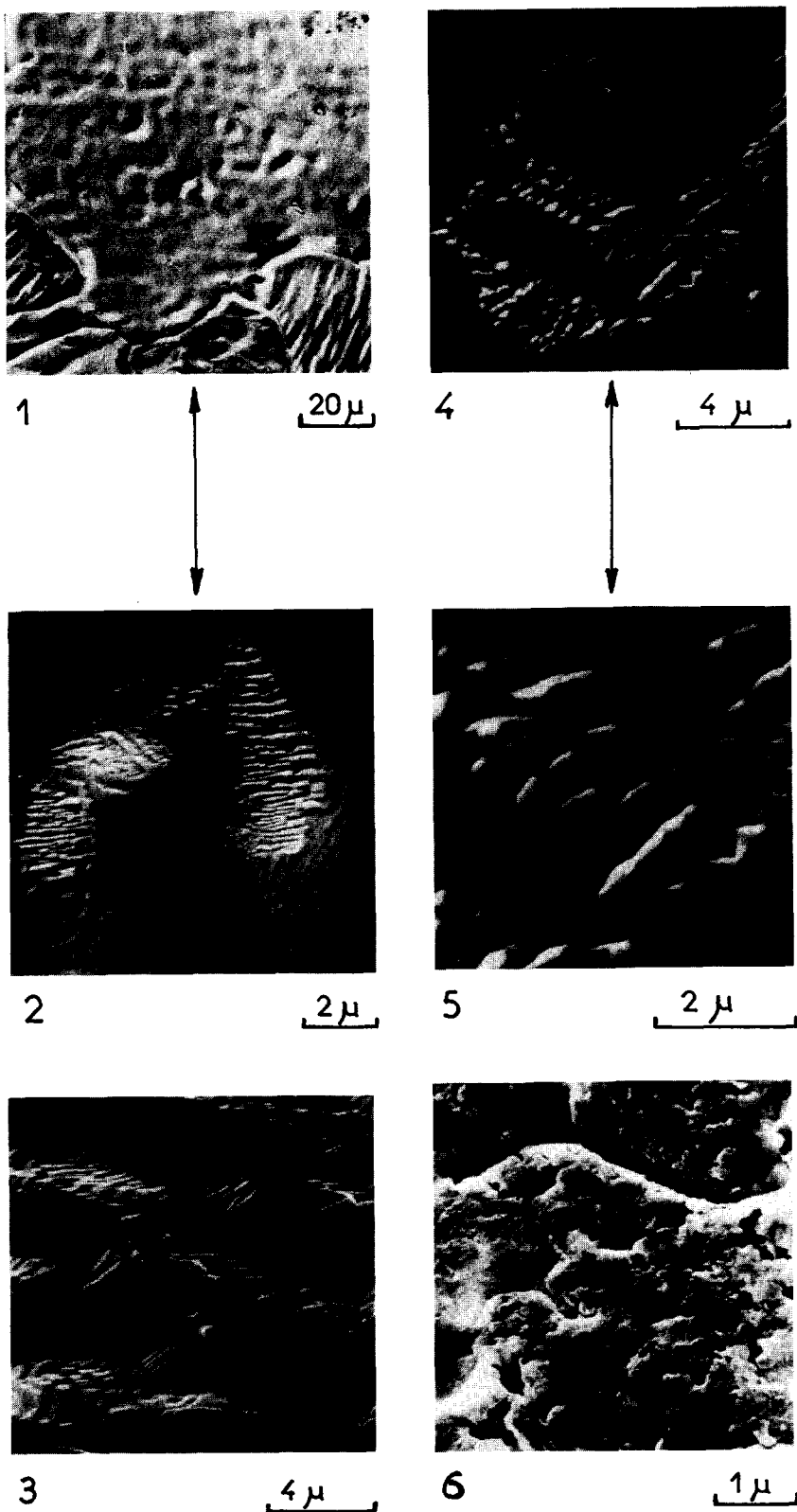


FIG. 14. Micrographs obtained by scanning electron microscopy of Rh ribbons first thermally (1-3) or mechanically (4, 5) polished before being subjected to the H_2-O_2 reaction; (see text for micrograph 6).

the work of Szymerska and Lipski (17) who have proved that H₂ can sometimes favour such a segregation. The Auger analysis allows us to give up this possibility in our case, probably because of the high H₂ pressure (compared to that used by the previous authors) which should be able to decontaminate the surface as the segregation occurred.

Attention must now be turned toward the possibility that there might exist some optimum O₂ coverage to favor the catalytic activity. Changes in catalytic activity would then merely reflect progressive changes of the oxygen coverage. Moreover, the completely deoxygenated metal surface should possess a very poor intrinsic activity.

However, in most of our experiments, we have measured the rate at which O₂ is reacted. It follows from the order of magnitude of this rate that the amount of O₂ consumed per second is usually much larger than one monolayer capacity so that the time needed by the O₂ coverage to follow a change of the gas O₂ content is much less than 1 sec. No observable transient could follow from so fast a change of the surface composition, unless the highest part of the activity concentrates on a very small fraction of the rhodium surface which could bind oxygen very strongly. The long deactivation which follows an oxidant pretreatment or a decrease of the oxygen content in the gas would then be due to the slow reduction of the strongest binding sites. However, what would remain unclear in this case is the reason why the increase of activity would not immediately follow that of the oxygen content (cf. Section 5b).

The experiments summed up in Figs. 12 and 13 make it possible to get a deeper insight into the nature of the oxygen effect which is best understood as the result of a dynamic situation where O₂ and H₂ react on the surface either in a continuous or in a sequential manner. This is especially obvious in Fig. 13 relating to a procedure which makes the surface composition the

same at the time of every probing of activity but according to which the progress in activation exactly follows every oxidation-reduction cycle and stops when the surface is exposed for a long time to O₂ only.

An important point which remains to be cleared up is the origin of the maximum displayed by curve 1 in Fig. 12. Even if, as expected, the same final steady state as in curve 2 is eventually reached, every long He-O₂ pretreatment leads to a memory effect of this kind. We think that the simplest way of explaining this behavior is to assume that a certain amount of O₂ is able to penetrate into the metal during the pretreatment. When the surface is then exposed to the reducing reactant mixture it is reduced (at least partially) and bulk oxygen can now slowly diffuse back to the surface and then contribute to some transient extraactivity. We shall report later (29) on other experiments which will convincingly exemplify this point. The possibility of incorporating O₂ into the bulk of transition metals has already been assumed and it has recently been referred to in the cases of Pd (30), Ru (31) and Rh (7, 21, 22). In this latter case, it has been pointed out that the O₂ dissolution begins at as low a temperature as 400 K (32).

At the moment, we are unable to explain the experimental facts as a whole by any other assumption than that of the *structural surface sensitivity to the H₂-O₂ reaction and the existence of labile active sites on the disturbed surface*. This view constitutes some kind of return to the original conception of active centers by Taylor (33) who identified them with extralattice atoms which could be produced by the adsorption of reactants. Taylor connected the higher reactivity of such atoms with their unsaturated character. However, in addition, and as Langmuir suggested (34), we may think of a disordered surface as being enriched with various atomic configurations and expect some of them to fit kinetic requirements in a better manner than others. The possibility of metal atoms being dislodged

from their usual lattice positions by oxidation-reduction cycles, thus allowing production of vacancies on the surface, has recently been put forward by Otero-Schipper *et al.* (10) to account for the effect of oxidant pretreatments. The deactivation under H_2 exposure has been explained by these authors as resulting from the thermal recovery of the lattice and this assumption falls exactly into line with ours. Kishimoto *et al.* agree with our explanation in the case of Pt (35) and Pd (36) activated by successive oxidation and reduction in oxidation of H_2 and C_2H_4 hydrogenation.

Our experiments show that the oxygen effect can also be displayed in a continuous way in the course of reaction and can thus be responsible not only for pretreatment effects but also for transients resulting from the change of any kinetic parameter. In agreement with our model the precise number of active sites on the surface in each situation depends to a large extent on the corresponding working conditions. When one or another condition is varied, a long time may be needed in order that the number of active centers exactly fits the new working conditions and this is the reason for the kinetic memory effects.

These remarks may be applied to the variation of activity versus temperature. It is a well known fact that C_2H_4 hydrogenation occurs at a maximum rate for some optimum temperature, which has been repeatedly verified either for the steady activities (Fig. 8) or for transient activities measured as a function of a linearly increasing temperature (Figs. 3 and 5). That the curves of variation of steady rates display a maximum against T can be explained as formerly (3) by the result of a competition between the production of active sites through the H_2-O_2 reaction and the thermal recovery of the surface. At a sufficiently high temperature nearly the entire O_2 content is reacted, so that the rate of production of active sites levels off whereas the surface recovery goes on increasing and becomes the prevailing process. That ex-

planation relates to the steady curves of Fig. 8. However, when nonsteady rates are measured as a function of a regularly increasing temperature, an additional fact may result in the occurrence of a maximum in the variation of the catalyst activity. The reduction of the preoxidized surface indeed occurs the faster as T increases thereby giving rise to a sudden production of labile sites. Such a transient extraactivity cannot be produced when decreasing the temperature and cannot contribute to the steady curves of Fig. 8. But it may explain the abnormally depressed zone displayed by curves A and B of Fig. 5.¹ Most significantly the same peculiarity occurs again when the H_2-O_2 reaction *alone* is proceeding in the same way (Fig. 6). The surface events which are responsible for these noticeable kinetic features thus turn out to be a metal/ O_2 / H_2 property which is merely reflected by C_2H_4 hydrogenation when the hydrocarbon is present.

All of the catalytic transient behavior may be explained in agreement with our assumptions. For instance, when the temperature is increased to near its optimum value or beyond, the initial and immediate increase of activity shows that the true thermal coefficient of the reaction is positive. However, soon afterward, the slow decreasing part of the kinetic response is due to the progressive resorption of active sites resulting from a higher increase in the rate of thermal restructuring as compared to that of the creation of active sites, since most of the O_2 content has been used up.

Another important kinetic feature is the difficulty of ascertaining that the steady state is well established. Very slow increases of activity may persist over several days and these are to be paralleled with the progressive faceting of the metal and the development of its roughness. However the

¹ It can also explain that two successive maxima of activity may be observed in C_2H_4 hydrogenation when an appropriate rate is chosen for the increase of temperature.

latter fact cannot be identified with the cause of the promoting effect because it is produced in a very progressive way and remains irreversible. In fact, this faceting—as well as the catalytic activation—is a consequence—and not a cause—of the O₂ effect. The catalytic activation is the direct consequence of the atomic mobility induced by the H₂-O₂ reaction whereas the faceting resulting from this mobility occurs on another scale and so needs a much longer time to appear and develop.

The question of the possible formation of carbonaceous residues on the surface, frequently referred to, also deserves to be mentioned. We shall revert to this point with more details in a later publication. What can now be reported is that much of the kinetic behavior of the catalyst can be explained in a qualitative way with no need for assuming a contamination of the metal by ethylenic residues. However, some experiments reveal that such a contamination does exist. An example is given by Fig. 4 where it can be seen that the deactivation occurs a little faster under the reactant mixture (curves 1, 2, 4) than under pure H₂ (curve 3). In the same way, when the deactivation following an activating treatment has slackened enough, substituting pure H₂ for the reactant mixture for a few minutes makes it possible to observe a small rate increase when coming back to the reaction conditions. Carbonaceous residues are therefore able to appear but then can react with H₂ in our range of temperature and some definite steady state results.

Moreover, another way for the chemisorption of C₂H₄ to interfere with the activation of the surface by the H₂/O₂ reaction and to play a part in the determination of the catalytic activity may be exhibited in a remarkable and unexpected manner on which we shall report later. It essentially consists in the ability of C₂H₄ to *strengthen* the activation of the surface by the H₂-O₂ reaction under certain conditions.

Finally, the present work leads to the conclusion that ethylene hydrogenation is a

structure-sensitive reaction. The same conclusion has been arrived at by other authors (39-41), but for different reasons. This point is also evident from the experiments of Beeck (12) since the activity of his evaporated metal films decreased much faster with annealing temperature than did their area. The high activity of such films can be largely ascribed to their highly defective initial state. The structure sensitivity of ethylene hydrogenation can also be derived from the work of Eckell (41) which related to the possibility of generating active sites by cold-working of the metal and which has been confirmed more recently by Kishimoto *et al.* (36) and Uhara *et al.* (42).

CONCLUSION

It emerges from the present work that oxygen is able to exert a large effect on the catalytic activity of massive rhodium in the hydrogenation of ethylene. Oxygen can be made to play its role either as a pretreatment agent or as an impurity contained in the reactant mixture. In either case, our experimental evidence favors an explanation of this effect based upon the structural sensitivity of the surface toward the H₂-O₂ reaction involving preadsorbed or gaseous oxygen. It is concluded that there is a chemical generation of active sites due to induction of atomic surface mobility by the H₂-O₂ reaction. Active sites are conceived as being continuously generated and destroyed in such a way that their exact number at any time depends closely on the sample history and on the working conditions.

Explanation of the O₂ effect in this way does not exclude that O₂ may serve as a decontaminating agent or that some strongly adsorbed oxygen may alter the surface properties, but it means that the phenomena reported here cannot be unravelled by such assumptions only.

ACKNOWLEDGMENTS

We are grateful to Dr. J. J. Ehrardt and Dr. M. Alnot for the production of Auger spectra, to J. Lambert for

his technical assistance, and to A. Kohler for taking scanning electron micrographs.

REFERENCES

1. Pareja, P., Amariglio, A., and Amariglio, H., *J. Chim. Phys.* **71**, 1199 (1974).
2. Amariglio, A., Pareja, P., and Amariglio, H., *J. Chim. Phys.* **71**, 1207 (1974).
3. Pareja, P., Amariglio, A., and Amariglio, H., *J. Catal.* **36**, 379 (1975).
4. Pareja, P., Amariglio, A., and Amariglio, H., *React. Kinet. Catal. Lett.* **4**, 459 (1976).
5. Pareja, P., Amariglio, A., Piquard, G., and Amariglio, H., *J. Catal.* **46**, 225 (1977).
6. Palmer, R. L., and Vroom, D. A., *J. Catal.* **50**, 244 (1977).
7. Sexton, B. A., and Somorjai, G. A., *J. Catal.* **46**, 167 (1977).
8. Somorjai, G. A., *Catal. Rev. Sci. Eng.* **18**(2), 173 (1978).
9. Smith, C. E., Biberian, J. P., and Somorjai, G. A., *J. Catal.* **57**, 426 (1979).
10. Otero-Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., and Cohen, J. B., *J. Catal.* **53**, 414 (1978).
11. MacCabe, R. W., and Schmidt, L. D., *Surf. Sci.* **60**, 85 (1976).
12. Beeck, O., *Disc. Faraday Soc.* **8**, 118 (1950).
13. Kouskova, A., Durand, E. M., Adamek, J., and Ponec, V., *Coll. Czech. Chem. Commun.* **34**, 2645 (1969).
14. Kouskova, A., Adamek, J., and Ponec, V., *Coll. Czech. Chem. Commun.* **35**, 2538 (1970).
15. Briggs, D., and Dewing, J., *J. Catal.* **28**, 338 (1973).
16. Schlatter, J. C., and Boudart, M., *J. Catal.* **24**, 482 (1972).
17. Szymerska, I., and Lipski, M., *J. Catal.* **47**, 144 (1977).
18. Bernasek, S. L., and Staudt, G. E., *J. Catal.* **45**, 372 (1976).
19. Grant, J. T., and Haas, T. W., *Surf. Sci.* **21**, 76 (1970).
20. Haas, T. W., Grant, J. T., and Dooley, G. J., *Phys. Rev. B.* **1**, 1449 (1970).
21. Tucker, C. W., *J. Appl. Phys.* **37**, 4147 (1966).
22. Tucker, C. W., *Acta Met.* **15**, 1465 (1967).
23. Meelheim, R. Y., Cunningham, R. E., Lawless, K. R., Azim, S., Kean, R. H., and Gwathmey, A. T., *Proc. Int. Congr. Catal., 2nd (Paris 1960)* **2**, 2005, Editions Technip, Paris, 1961.
24. Roginskii, S. Z., Tret'yakov, I. I., and Shekhter, A. B., *Dokl. Akad. Nauk SSSR* **91**, 881 (1953).
25. Flytzani-Stephanopoulos, M., Wong, S., and Schmidt, L. D., *J. Catal.* **49**, 51 (1977).
26. Chao, F., Costa, M., and Tadjeddine, A., *Surf. Sci.* **46**, 265 (1974).
27. Schmidt, L. D., and Luss, D., *J. Catal.* **22**, 269 (1971).
28. Poltorak, O. M., and Boronin, V. S., *Russ. J. Phys. Chem.* **40**, 1436 (1966).
29. Amariglio, A., Lakhdar, M., and Amariglio, H., *Proc. Int. Congr. Catal., 7th (Tokyo 1980)*, in press.
30. Campbell, C. T., Foyt, D. C., and White, J. M., *J. Phys. Chem.* **81**, 491 (1977).
31. Reed, P. D., Oomrie, C. M., and Lambert, R. M., *Surf. Sci.* **64**, 603 (1977).
32. Thiel, P. A., Yates, J. T., Jr., and Weinberg, W. H., *Surf. Sci.* **82**, 22 (1979).
33. Taylor, H. S., *J. Phys. Chem.* **30**, 145 (1926).
34. Langmuir, I., *Trans. Faraday Soc.* **17**, 621 (1921).
35. Kishimoto, S., and Norimatsu, A., *J. Chem. Soc. Japan* 565 (1976).
36. Kishimoto, S., Yoshimoto, Y., Nakajima, T., and Hatayama, T., *J. Chem. Soc. Japan* 1003 (1979).
37. Bond, G. C., "Catalysis by Metals," p. 243. Academic Press, London and New York, 1962.
38. Pajonk, G., and Teichner, S. J., *Bull. Soc. Chim. Fr.* **1971**, 4235 (1971).
39. Pajonk, G., and Teichner, S. J., *Bull. Soc. Chim. Fr.* **1971** 4242 (1971).
40. Dalmai-Imelik, G., and Massardier, J., *Proc. Int. Congr. Catal., 6th (London 1976)*, 90. Chemical Society, London, 1977.
41. Eckell, J., *Z. Elektrochem.* **39**, 433 (1933).
42. Uhara, I., Kishimoto, S., Hikino, T., Kageyama, Y., Hamada, H., and Numata, Y., *J. Phys. Chem.* **67**, 966 (1963).