

CATALYTIC ACTIVATION OF RHODIUM, REVEALED BY C_2H_4 HYDROGENATION AND RESULTING FROM PRE-INCORPORATION OF O_2 AND BACK-DIFFUSION TO ITS SURFACE UNDER H_2 EXPOSURE

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ABSTRACT : Strong activations in C_2H_4 hydrogenation are induced by pretreating a Rh ribbon with He- O_2 mixtures. The strength of activation observed at a reference temperature (200°C) does not depend on the O_2 content but increases with the length and temperature of pretreatment, strongly suggesting that Rh incorporates O_2 . Direct evidence is given for this incorporation. Several noteworthy kinetic features indicate that the main variable to be considered in this activation is the flux of O_2 back-diffusing to the surface under a reducing flux of H_2 or reactant mixture. The activation is explained by the production of active centers when O_2 is extracted from the surface by H_2 whereas deactivation would occur because of the thermal restructuring of the surface.

1. INTRODUCTION

We have previously shown ^{1 to 4)} that O_2 traces contained in $H_2 + C_2H_4$ mixtures can exert a strong promoting influence upon transition metals that are classically used as catalysts for this typical hydrogenation. That influence is displayed at high enough temperatures (currently > 100°C) so that H_2 can react with adsorbed oxygen and so prevent the metal surface from excessive coverage. The activating effect can also be evidenced when O_2 has been able to accumulate on the surface during a pretreatment ^{1,2,4)}. The latter effect has also been observed by other authors in the case of this reaction ^{5,6)} or other ones ^{7 to 13)}. The O_2 influence has been interpreted as a cleaning of the surface from carbonaceous residues ^{5,6)} or as the induction of a better activity by O atoms remaining on the surface or in the near-surface region, even under reacting conditions ^{7, 9 to 11)}.

In our particular case we have shown that both interpretations are at variance with several aspects of the catalyst behavior and we have proposed ^{1,2,4)} a new explanation based upon the atomic

surface mobility which is caused by the H_2-O_2 reaction. That mobility has been shown only at a macroscopic scale^{4,14)} but the rearrangement observed must obviously be the eventual consequence of atomic dislodgements. We suggest that some of the various configurations which are then expected to appear possess an especially high catalytic activity. The number of such active sites would then result from a balance between their rate of chemical generation and that of their disappearance by thermal restructuring of the surface.

In the case of Rh, some kinetic features previously reported⁴⁾ prompted us to think that, even at low pressures, the metal is able to incorporate O_2 which can then back-diffuse to the surface under the reacting conditions. The present work has been undertaken in order to get a deeper insight into this possibility.

2. EXPERIMENTAL

The kinetic measurements are performed in a flow-type apparatus already described elsewhere^{1,4)}. The gases are carefully purified and the reactant mixture is always 5 % C_2H_4 in H_2 . After purification all the gases may be enriched with O_2 . The O_2 content of the gases can be measured with the use of an electrochemical O_2 meter (ENGELHARD, HERSCH MARK II). The extent of the reaction is known from a chromatographic analysis. The catalyst may be conveniently flushed with He, He- O_2 , H_2 , H_2-O_2 , $H_2 + C_2H_4$ or $H_2 + C_2H_4 + O_2$. It consists of a rhodium ribbon (HERAEUS; 99.99 % purity), 3/100 mm thick, 1 mm wide and 2 cm long.

A.E.S. and X.P.S. analyses have been performed with a LEYBOLD-HERAEUS spectrometer equipped with a preparation chamber which may be fed with gases at atmospheric pressure. The sample may be quickly transferred from it into the analysis chamber while being maintained under vacuum.

3. SYSTEMATIC STUDY OF THE PRETREATMENTS

3.1. Experimental procedure

We have first carried out various pretreatments by He- O_2 mixtures under more and more oxidizing conditions in order to reach a more complete knowledge of the effect under study and to know its controlling factors. In order to make comparisons meaningful, the catalyst was previously deactivated under ultra-pure H_2 at 400°C, so that its remaining activity at 200°C decreases down to a negligible value, before being pretreated. The catalyst behavior which results is observed at a reference temperature of 200°C as this reaction presents a maximum rate near to this temperature. In order to protect the surface as well as possible against the contaminating influence of the hydrocarbon, the metal is continuously fed with ultra-pure H_2 and

its activity is monitored in a discontinuous way only, by periodically flushing the catalyst, for 30 s. only, with the reactant mixture deprived of any O₂.

3.2. Typical evolution of the activity after an He-O₂ treatment

A typical variation of the catalytic activity against time after an He-O₂ treatment is displayed for example by curve 1 of Fig. 1. The activity passes through a maximum after 1 or 2 hours. A very long time is needed in order that the activity level decreases to its initial very low value ;(typically more than 20 hours are needed in order that the remaining activity decreases to half its maximum value).

The various factors which are expected to control the activation of the catalyst are the O₂ content of He, and the length and the temperature of the pretreatment. We shall examine them in turn.

3.3. Influence of the O₂ content

In spite of some irreproducibility and taking into account the large extent of variation of O₂ content (more than a factor of 300) it can be concluded from Fig. 1 that the O₂ content does not affect the pretreatment efficiency, at least for O₂ contents of these orders of magnitude.

3.4. Influence of the exposure length

From Fig. 2 it clearly appears that the catalyst activation strengthens if the exposure length is increased and the maximum activity occurs later. Moreover the deactivation takes place more slowly.

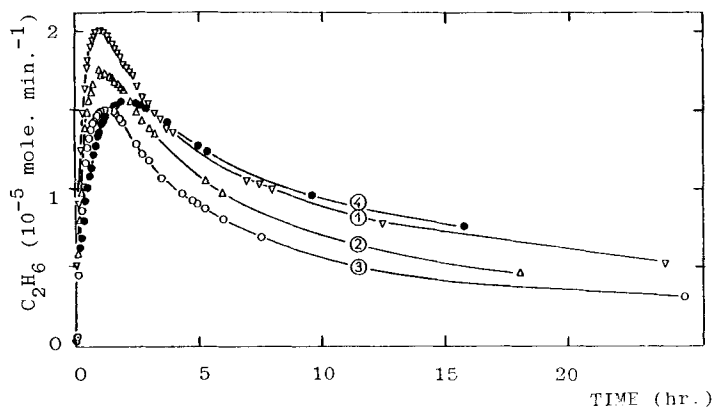


Fig. 1. Variation of catalytic activity at 200°C, as a function of time after a flush of 1 hr. at 200°C by He-O₂ mixtures. O₂ content of He-O₂ : 15.5 p.p.m. (curve 1) ; 80 p.p.m. (curves 2 and 3) ; 5000 p.p.m. (curve 4).

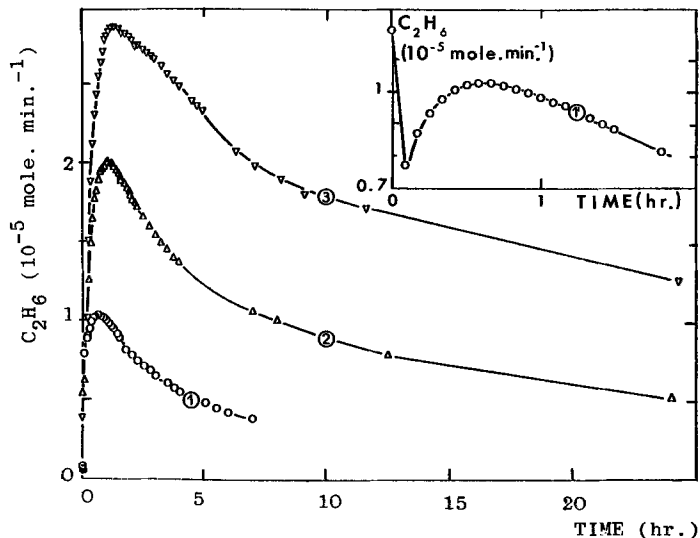


Fig. 2. Variation of catalytic activity at 200°C, as a function of time after flushes of different lengths by He-16 p.p.m. O_2 at 200°C.

Period of exposure : 10 min. (curve 1) ; 1 hr. (curve 2) ; 15 hr. (curve 3).

Fig. 2 (curves 1 and 1') shows also that for mild oxidizing treatments, the initial behavior of the catalyst is somewhat more complex than that is displayed in Fig. 1.

3.5. Influence of the temperature pretreatment

Stronger activation can be obtained if the O_2 exposures are performed at higher temperatures as is visible in Fig. 3. But, most notably, as soon as the pretreatment temperature reaches 350°C, the preceding maximum is replaced by a plateau of constant activity.

Any further increase in the pretreatment severity results in longer plateaux without any further significant change of their height. If the pretreatment is effected during one hour at about 500°C the plateau is observed during more than 10 hours and more than one week would be required to deactivate the sample at 200°C. If the pretreatment temperature is still increased, the results remain mainly the same and longer plateaux are obtained. But there is a tendency towards a slight decrease in their height and an increase in the exposure time to H_2 is required to get them established.

4. DIRECT EVIDENCE FOR THE O_2 INCORPORATION

4.1. Measurement of O_2 absorption

The rate of the O_2 incorporation is expected to be low at such

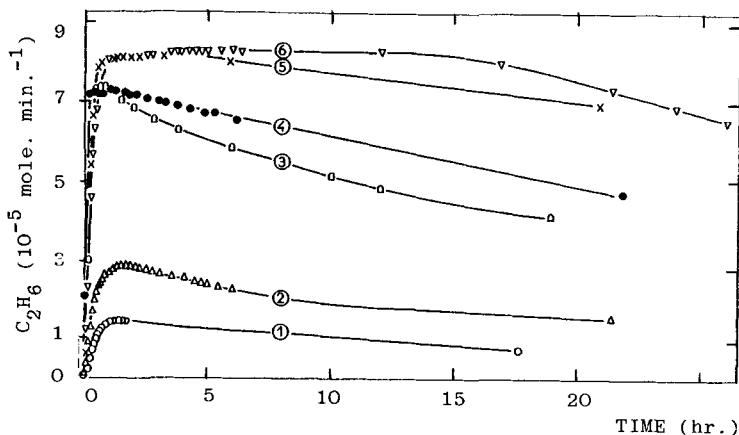


Fig. 3. Variation of catalytic activity at 200°C, as a function of time after a flush of 1 hr. by He-15 p.p.m. O₂ at increasing temperatures.

Pretreatment temperature : 200°C (curve 1) ; 300°C (curve 2) ;
 350°C (curve 3) ; 400°C (curve 4) ;
 450°C (curve 5) ; 496°C (curve 6).

moderate temperatures but we have tried to detect it by using the O₂ trace analyser. In order to get the highest sensitivity, the O₂ content of He has been lowered to only 4 p.p.m.

Fig. 4 reports the difference Δ between the O₂ contents at the inlet and outlet of the reactor plotted against temperature, during application of a thermal linear increase of 8°/min. Prior to the flushing of Rh with He-O₂, the sample has been deactivated by subjecting it to H₂ at 400°C and has then been flushed with pure He at the same temperature in order to extract the H₂ which might have been dissolved into the metal. Experiment shows that no significant change occurs in the curve of Fig. 4 once the exposure to pure He exceeds one hour. The thermal decrease is then effected under pure He. This experiment shows unequivocally that O₂ incorporation begins at temperatures as low as 100°C and is in agreement with previous observations^{15,16}). At any time during the experiment, if the thermal increase is stopped and the temperature maintained constant, the O₂ consumption drops quickly. That the incorporation is still proceeding can nevertheless be evidenced by closing the reactor for some minutes. When the flush of gas is re-established, the O₂ meter clearly denotes a decrease in the O₂ content.

4.2. X.P.S. and A.E.S. analyses

A second type of experiment has been undertaken in order to

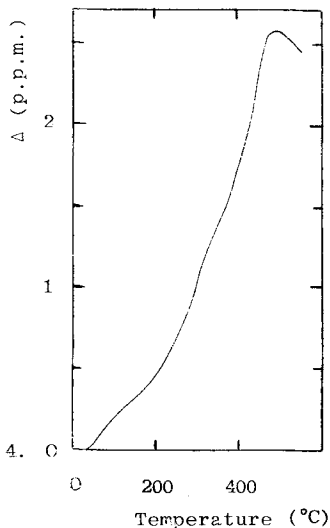


Fig. 4. C

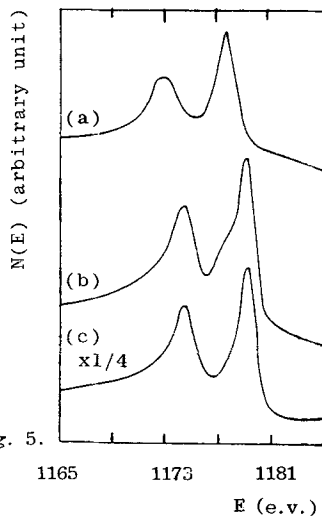


Fig. 5.

Fig. 4. Variation with temperature of the difference Δ between the O_2 contents at the inlet and outlet of the reactor flushed by He-4 p.p.m. O_2 (temperature increased at $8^\circ/\text{min.}$).

Fig. 5. $3d\ 3/2 - 3d\ 5/2$ X.P.S. spectrum of Rh.

a) after a flush by O_2 (15 hrs. ; 1 atm. ; 370°C).

b) after (a), followed by a flush by H_2 (15 min. ; 1 atm. ; 150°C).

c) after an Ar^+ bombardment ($\approx 1\ \mu\text{A}$; 15 min. ; 25°C).

detect any oxide formation by means of photoelectron spectroscopy. After having been exposed at 1 atm. of air, for 15 hours at 370°C , the sample is examined by means of X.P.S. (Fig. 5 ; curve a) and A.E.S. analyses. The $3d\ 3/2 - 3d\ 5/2$ X.P.S. peaks of Rh are shifted (1.4 to 1.6 e.v.) in comparison with the corresponding peaks after an ion bombardment ($\approx 1\ \mu\text{A}$ de Ar^+ ; 15 min.) (Fig. 5 ; curve c). Similarly the A.E.S. spectrum contains one supplementary peak near the main one (≈ 300 e.v.). Submitting the sample for 15 min. at 150°C to 1 atm. of H_2 is nearly sufficient to reduce the oxide (no more shift in the X.P.S. spectrum, as denoted on curve b, Fig. 5 ; no more supplementary peak in the A.E.S. spectrum). Nevertheless the O peaks are still high, in A.E.S. as well as in X.P.S.

5. MODE OF CATALYST DEACTIVATION UNDER H_2 EXPOSURE

A very long time is required to get the metal deactivated once it has been pretreated, especially if the pretreatment was strong.

In order to speed it up, the H₂ exposure may be carried out at temperatures higher than 200°C. Returning the sample to 200°C reveals a large extent of deactivation but if the operation is repeated, a new activation may appear which cannot continue at 200°C. Fig. 6 shows that the same thing can be repeated several times. If the H₂ exposure at 400°C is maintained several days, it becomes deactivating again. The H₂ exposure can then be made reactivating if it is carried out at a still higher temperature and it would eventually become again deactivating.

6. DISCUSSION

We can first conclude from this work that very strong catalytic activations can be obtained by He-O₂ treatments.

The lack of relationship between the activating power of He-O₂ mixtures and their O₂ content is easily understood as the result of the rapid coverage of the surface by O₂. That the strength of activation is nevertheless directly related to the length or the temperature of pretreatment strongly suggests that O₂ is penetrating into the metal and that higher amounts of O₂ are incorporated when either of these factors is increased. The ability of Rh to incorporate O₂ has already been established^{8,15,16} and we have added two pieces of direct evidence for that. Fig. 4 is in good agreement

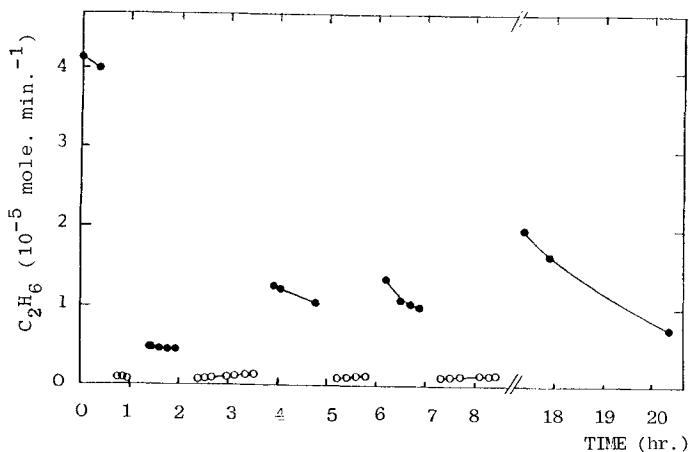


Fig. 6. Variation of catalytic activity as a function of time during a flush of H₂, either at 200°C (●) or 400°C (○). Initial pretreatment of the catalyst: exposure to a flush of (He-15 p.p.m. O₂) (1 hr.; 350°C), followed by a flush of H₂ (19 hrs.; 200°C).

with previous work ¹⁵⁾ as to the low temperature at which O_2 penetration begins. It may also be used to estimate the amount of O_2 incorporated during the time of the experiment (15×10^{-6} g. O_2 or 3 % of the sample thickness being oxidized as hypothetical RhO). The question now is to know how O_2 can activate the catalyst.

As the sample is maintained under ultra-pure H_2 except for the very short time of activity measurement, its deactivations (and reactivations) cannot convincingly be regarded as a matter of contamination (and decontamination). The assumption of the catalyst activity being strongly influenced by O_2 present in the near surface region seems to be favoured. But as the catalyst activity passes through a maximum against time when pure H_2 is substituted for $He-O_2$ one might be led to suppose that an optimum O_2 content ought to be present in the surface region for the activity to reach its highest possible value. The rising parts of the curves of Fig. 1,2,3 should then result from the surface getting rid of an O_2 excess. However such an assumption must be discarded since every increase in the strength of oxidation results in a steeper evolution and a higher level of catalytic activity.

It appears more convincing to think that a large part of the Rh surface is quickly reduced under H_2 (in agreement with X.P.S. analysis) and that the activity increase is due to the back-diffusion of pre-incorporated O_2 . The feed of the surface with O_2 from the bulk would not prevent the surface O_2 content from decreasing (or remaining steady momentarily) but would increase the number of active centers by reaction with H_2 in agreement with our previous views. The activation of the sample must then reach some maximum as the O_2 feed slows down and the active centers spontaneously disappear.

Such a view is made still more plausible if one takes into account two other important facts : the complex evolution displayed after a mild pretreatment (curve 1', Fig. 2) and the occurrence of a plateau following a sufficiently severe pretreatment.

The complex evolution of Fig. 2 originates in a rather good separation between purely superficial events and diffusion from the bulk. It may indeed be thought that the reduction of the surface must happen before O_2 begins to diffuse. This fast reduction results in a production of active centers and the beginning of their spontaneous disappearance can be observed if it does not interfere with too strong a reactivation from O_2 back-diffusion.

As to the most noteworthy display of a plateau of constant activity one can easily imagine that as soon as the pretreatment is severe enough, a relatively thick oxide layer builds up and constitutes an O_2

reservoir of constant composition. A steady-state concentration profile would result and the surface would then be fed with a constant O₂ flux. Such a constant flux of segregation has already been observed in the case of S diffusing to the surface of an iron sample¹⁷⁾.

When the sample is heated, the rate of O₂ diffusion is expected to increase faster than the thermal restructuring of the surface. We can therefore find there the reason for the complex catalyst behavior which is observed under H₂ exposure at a higher temperature (Fig. 6). Any thermal increase first speeds up the deactivation of active centers which have been formed at lower temperature by using underlying O₂. But diffusion from a deeper region is accelerated too and results in a new activation as soon as the increased O₂ flux reaches the surface. Returning to the reference temperature makes the activation visible but slows down the diffusion process and the number of active centers cannot be maintained. The deactivation rate is even higher than if the sample had not been heated. If the sample temperature is increased again, a reactivation may be observed, but this reactivation eventually gives place to deactivation when O₂ diffusion has slackened enough. Reactivation may however be observed once more if the temperature is still increased. Experiment shows that weeks of exposure to pure H₂ may be required in order that the sample definitely deactivates and a very low activity is eventually reached.

It is highly tempting to compare the main results of this work with those obtained by Burwell et al.¹²⁾ in another case. These authors have also explained their results by assuming that lattice distortions occur when O₂ reacts with H₂ on the surface but they have considered that the reactivation under H₂ at elevated temperatures could not be reconciled with this view. However they may have overlooked the possibility for the pre-incorporated O₂ to back-diffuse to the surface under those H₂ exposures.

7. CONCLUSION

Very strong catalyst activations may result from pre-incorporation of O₂ into the metal lattice inasmuch as back-diffusion is allowed under reacting conditions. The flux of back-diffusing O₂ seems to be the main factor which must be considered in order to explain all of the noteworthy features of the catalyst behavior. That completely fits with our previous conclusions which related to the case where O₂ comes from the gas. According to these the surface is maintained out of equilibrium with respect to its defect content through the continuous extraction of O₂ by H₂. The same

would occur here and deactivation would also happen because of the thermal restructuring of the surface.

It follows that the bulk has to be regarded as a part of the environment of the catalyst surface in that it may largely contribute to sustain its catalytic activity.

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DISCUSSION

W. Palczewska (Inst. Phys. Chem., Warszawa)

A more detailed interpretation of physical nature of those active centers would perhaps be possible on the basis of a study under well-determined metal surface conditions. Such conditions might be single crystals, instead of polycrystalline ribbons with their cleanliness strictly controlled by AES. Prolonged exposure to gases (as well as to vacuum as in the study) could contaminate the sample surface; heating could separate common impurities to grain boundaries.

- 1) Have you some idea concerning the physical nature of the active centers which appear and disappear on the surface of Rh?
- 2) Did you observe a similar phenomenon of the activating

effect induced by pre-incorporated oxygen in the case of other metals able to solve oxygen (Ni, Pt, Ru etc; particularly in connection with the preceding A 46 results)?

A. Amariglio

As reported, we have examined our Rh sample by means of A.E.S. spectroscopy after a quick transfer from the preparation chamber into the analysis one. The impurities initially detected were C, S, Ca and P. When the metal is flushed by pure H₂ at 300°C and under atmospheric pressure, it progressively purifies itself of S, P and Ca. C is slowly and less completely removed by H₂ but reacts with O₂ easily so that a sequence of 6 to 10 oxido-reduction treatment at 400°C and under atmospheric pressure makes it possible to clean the sample. When it is then maintained overnight at the same temperature under vacuum or under a flow of H₂ no further contamination can be detected. We can so be sure that the deactivation we observe during the prolonged exposure to pure H₂ is not due to contamination effects.

The same kind of experiments could be carried out upon single crystals and would lead to a detailed observation of the behavior of faces with different orientations but would not result in a deeper understanding of the physical nature of the active centers. All we can say at the moment is that the metal surface is certainly disturbed by the H₂-O₂ reaction as is clearly evidenced by the gross surface rearrangement which occurs in the long run (J. Catal. submitted to). As the surface rearrangement must obviously be the result of the mobility which is induced at the atomic scale, various atomic configurations appear and disappear. Their amount is maintained out of equilibrium by the H₂-O₂ reaction. We think it reasonable to assume that some of these configurations may serve as active centers. Are they vacancies, bi-vacancies, kinks or adatoms? We do not know.

A similar phenomenon has been observed in the case of Ni, Cu and Pt but we have yet no data concerning Ru.

A. Baiker (Swiss Federal Inst. Tech., Zurich)

Due to the exothermicity of the reaction of hydrogen with the surface oxide layer it could be possible that the surface temperature is considerably higher than the bulk temperature and as a secondary effect this phenomenon could also contribute to the higher activity of the pretreated Rhodium-sample.

My questions are therefore: How was the temperature of the Rhodium ribbon measured during the experiments and do you have

evidence that this temperature effect can be neglected? I believe that differential scanning calorimetry-measurements could reveal this particular point.

A. Amariglio

The temperature is measured using an Fe-Cr thermocouple placed against the rhodium ribbon but separated from it by the means of a silica tube (1/8" outside diameter). The thermocouple indication is permanently recorded.

The temperature so-measured may not be the exact temperature of the ribbon and particularly of its surface. When the catalyst, first oxidized by (He, O₂), is submitted to a flow of H₂, the measured temperature initially varies within an extent of a few degrees but after some minutes remains constant. The true temperature is expected to display the same behavior. As our experiments last more than 10 or 20 hours, the large variation of activity could hardly be fully ascribed to thermal changes.

Moreover, in that particular case, there is a strong reason to discard any thermal effect as a possible explanation of the enhancement of activity. It is well known that this reaction displays a maximum rate at nearly 200°C. Any increase of the temperature would have resulted in a lowering of the rate. More precisely, when the catalyst temperature is increased from 200 to 250°C, the activity is decreased by nearly 40%. So we can state that if there is an increase of the surface temperature due to the exothermicity of the reaction, the catalyst activation is still stronger than that we have observed.

I.P. Wilson (Union Carbide, South Charleston)

The enhanced activity of your O₂-treated foils may be due to O²⁻ ions on their surface. One means of stabilizing and oxidized Rh species on the surface of the metal during hydrogenations would be to form a surface compound with an irreducible cation. It was suggested earlier at this meeting that Mg and Mn form such compounds. Have you or do you plan to study the effects of these or other added cations in your system?

A. Amariglio

The enhancement of the catalyst activity by the presence of O₂ on the surface (no matter its true chemical state) would indeed explain the shape of the evolution of the catalyst activity as a function of time. The optimum activity would then be explained by the attainment of some optimum O₂ coverage.

However such an assumption must be discarded since every increase in the strength of oxidation results in a steeper evolution and a higher level of catalytic activity.

Furthermore in other experiments which will be published elsewhere (submitted to J. Catal.) we have shown, in the case of activation by gaseous O₂, that it is the repetition of oxidation-reduction processes on the surface which is the true cause of activation and not the mere exposure to O₂. For instance the sample of Rh is more activated by exposure to an H₂-O₂ mixture for 1/4 hour than by an exposure to an He-O₂ mixture for 22 hours. The main part of the activation is induced by the H₂-O₂ reaction and not merely by the presence of O₂ on the surface. We conceive it as the result of the embedding of O₂ on the surface followed by its extraction with H₂.

So, if Mg and Mn stabilize the oxidized Rh and as a consequence maintain O₂ on the surface, the addition of these cations to our system would not lead to an enhancement of the catalytic activity, at least from this point of view.

Y. Schachter (Univ. Bar-Ilan, Israel)

Several years ago, Prof. Pines shows that Ni and Pt-metal catalysts prepared under conditions where small amounts of oxide are present, are active in dehydration of alcohols, by a mechanism where O²⁻ acts as a Lewis base. Have the authors considered the possibility of a mechanism where O²⁻ could play a part?

The metals by themselves are, of course, known as hydrogenation catalysts. The dehydration experiments mentioned above were carried out in a hydrogen current.

A. Amariglio

We have just explained in our reply to the former question that the mere presence of O₂ on the surface cannot explain the main part of the catalytic activation of Rh.