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Effect of Oxidizing Pretreatments on the Behavior of a Rhodium Powder in CO_2 Chemisorption and Methanation

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The effect of preoxidation on the catalytic behavior of a sample of Rh powder was examined. Prior to any oxidation the sample showed activity at $T \geq 140°C$ with an activation energy of 18.5 kcal/mole. Preoxidation of the powder conducted at $T \geq 200°C$ resulted in strong though transient activations, the major portion of them appearing below 100°C. There was excellent agreement between reduction of the oxidized sample and induction of the extra activity, as was also the case for a Rh ribbon. The freshly reduced surface was correspondingly modified in its chemisorption behavior. The facts are explained in terms of transient distortions of the metal lattice appearing in the course of the reduction process.

INTRODUCTION

It has already been shown that the catalytic activity of metals can be strongly improved either by inclusion of O_2 traces in the reactant mixture in the case of C_2H_4 hydrogenation (*1–4*) or by oxidizing pretreatments in various hydrogenations (*4–22*). Different explanations have been proposed. We have reported experiments which were designed to discriminate between them (*4*). Some observations were best explained with the assumption that reduction of the preoxidized surface results in a transiently distorted and therefore more active catalyst. This assumption did not preclude that O_2 could burn off contaminants or exert a promoting effect by itself. However, both of the latter possibilities fail to explain all of the experimental facts.

We recently reported on the behavior of a Rh ribbon in the methanation of CO_2 (*22*). No activity could be observed on the well-reduced and clean catalyst. As the sample had but a very small area (0.2 cm^2), it was interesting to extend our study to the case of the same metal but in the form of a powder. The latter was chosen as a means of studying the behavior of the metal in a state of higher dispersion but without any support as a first step. The present article reports on the results thus obtained. Significant differences emerged and new experimental facts could be collected due to the greater area of the sample and its different morphology. In return these results prompted us to look for the possible extension of some of them to the ribbon. The latter was therefore briefly restudied.

EXPERIMENTAL

Kinetic measurements. Experiments were performed in a flow-type apparatus operated at atmospheric pressure whose essential features have already been described (*4*). Before being added to purified H_2, CO_2 was passed over CuO at 200°C (oxidation of CO traces) and a deoxo catalyst. The reactant mixture (H_2 + 5% CO_2) was then passed through a trap filled with glass beads which was maintained at dry ice temperature. The reactor was made of a tube of quartz equipped with a disk of fritted silica supporting the catalyst powder. Temperature was measured by means of a thermocouple located in a well projecting into the bed. At the reactor outlet, part of the reacted mixture was fed to the sampling valve

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of the gas chromatographs (FID or TCD) while the remainder was passed through an electrolytic Beckman hygrometer. The latter could measure H_2O content in the range 1–1000 ppm.

During preoxidation carried out with oxygen-doped He, an oxygen meter (Engelhard Mark II electrochemical meter) was used which allowed measurement of oxygen content in the range 1–100 ppm.

When CO was looked for in the reaction products and could not be detected by TCD the chromatographic analysis was modified as follows. H_2 instead of N_2 was used as the carrier gas in the chromatograph, and at the column exit the gases were directed toward a short tube maintained at 400°C and filled with 1 g of Co powder on which CO, if present, could be reacted into CH_4. CO could thus be easily detected at the ppm level by FID.

Catalyst. The catalyst was 0.6 g of Rh powder (Johnson Matthey specpure Rh sponge, 30 ppm total impurity, 10 ppm metallic impurity) with a specific area of 0.8 m^2 g^{-1} as determined by physical adsorption of Kr at 77 K. It was placed in the annular space lying between the outer wall of the reactor and the internal thermometric well. The catalyst bed therefore displayed the shape of a cylindric ring 0.4 cm high and with outer and inner diameters of 1.2 and 0.4 cm, respectively (cross section of the bed: 1 cm^2).

RESULTS

Intrinsic Activity of the Rh Powder

The first treatment to which the powder was submitted consisted of a number of alternate feeds with pure H_2 or a mixture of He + 20 ppm O_2 and this treatment was effected at 400°C. After each exposure to H_2 the activity of the powder was measured at the same temperature. Only a few alternate feeds were necessary to obtain a constant level of activity. Prolonged exposure (15 h) to H_2 at 400°C was then shown to exert no further effect upon the metal activity, and the kinetic examination was begun.

All the kinetic measurements reported here were obtained with a reactant mixture (H_2 + CO_2) containing approximately 5% CO_2 in every case. The reaction rate was often studied as a function of temperature during a temperature ramp of 6 K min^{-1}. The main products of reaction were CH_4 and H_2O. CO was also produced but at a slower rate (eight times less CO than CH_4 at 400°C, for example). Variations in CH_4 and CO production rates and variations in CO_2 molar flow rate at the reactor outlet as a function of temperature are reported in Fig. 1 (from nearly 250 to 500°C). CH_4 could be detected at as low a temperature as 140°C ($\simeq 1.1 \times 10^{-9}$ mol min^{-1}) and the variations in its production rate versus temperature in the low temperature range are given by curve 1 of Fig. 2. The activation energy which could be deduced from curve 1, Fig. 1 (and plot 1, Fig. 2 in the low temperature range) was 18.5 kcal/mol and compared well with the value given by Sexton and Somorjai (*11*) for a Rh ribbon (16 kcal/mol)

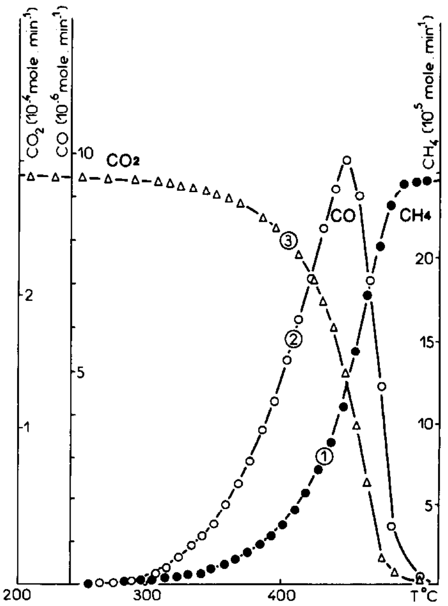

FIG. 1. Variations in the rates of CH_4 (curve 1) and CO (curve 2) production versus temperature. Curve 3 gives the simultaneous variation in the CO_2 molar flow rate at the reactor outlet. Rate of heating: 6 K min^{-1}.

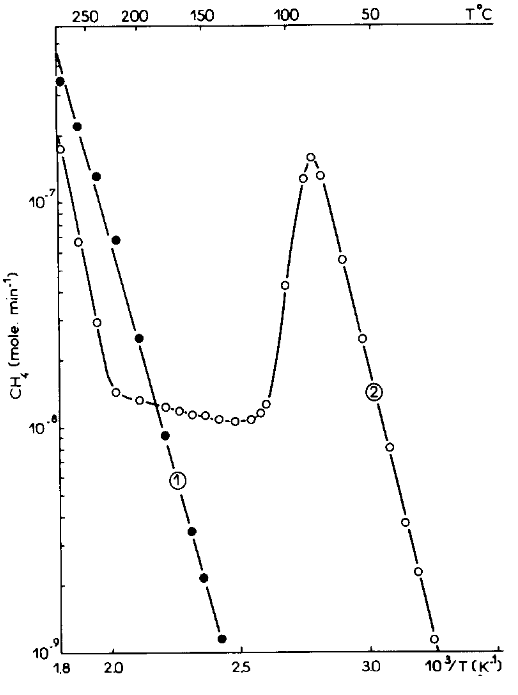

FIG. 2. Arrhenius plots in the low temperature range determined after exposure to H_2 (15 h, 400°C) (curve 1) or after oxidation (1 h, air, 400°C) (curve 2). Rate of heating: 6 K min^{-1}.

and that of Solymosi, Erdöhelyi, and Bánsági (*23, 24*) (16.2 to 19.4 kcal/mol) or Iizuka *et al.* (*21*) (15 to 23 kcal/mol) for supported rhodium.

From Fig. 1 CO production can be observed to pass through a maximum which coincides with the inflection point of the CO_2 curve at nearly 450°C. Similar results were obtained by Luengo *et al.* for the same reaction catalyzed by intermetallic compounds, Co or Ni powders (*25*). CH_4 production seems to be less affected than CO production by the CO_2 depletion. Nevertheless the Arrhenius plot corresponding to CH_4 production is linear between 220 and 420°C but begins to depart from the straight line in the neighborhood of the above inflection point.

Effect of Oxidizing Pretreatments

No activation effect resulted from either the introduction of small oxygen doses into the reactant mixture or the continuous presence of oxygen at an impurity level (a few ppm) throughout the entire temperature range explored. This result differed significantly from what was observed in the case of C_2H_4 hydrogenation over a Rh ribbon (*4*).

However, activating effects resulted from oxidizing pretreatments when they were strong enough. Figure 3 reports the results of oxidizing pretreatments of the powder conducted at 400°C with flowing air

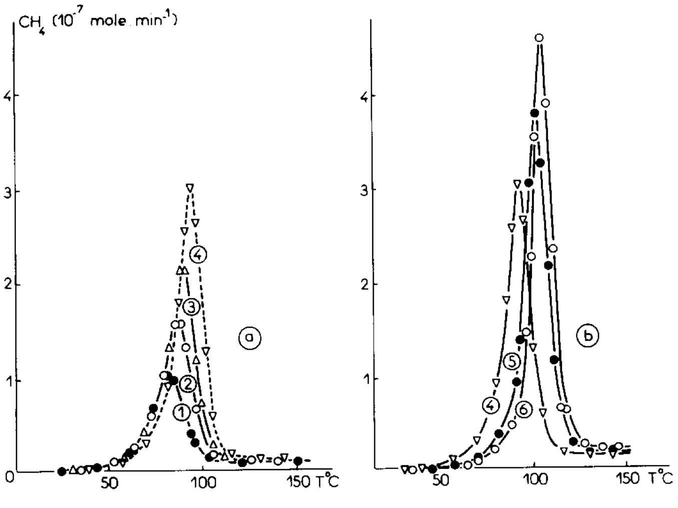

FIG. 3. Influence of the time of preoxidation by air at 400°C upon the variation of the resulting methanation activity as a function of temperature: 30 min (curve 1), 1 h (curve 2), 2 h (curve 3), 4.5 h (curve 4), 14 h (curve 5), 45 h (curve 6). Rate of heating: 6 K min^{-1}.

for periods of increasing length. Prior to each oxidation the metal was fed with flowing H_2 for 15 h at 400°C. Following each oxidation the catalyst was cooled under flowing helium to room temperature. Periods of air and H_2 or $H_2 + CO_2$ feeds were separated by short He flushes. The catalytic effects of preoxidation were observed whereas the catalyst temperature increased at 6 K min^{-1}.

The preoxidized Rh powder allowed the production of CH_4 to be observed at as low a temperature as 40°C. The rate displayed a maximum value at a temperature lying between 84 and 106°C according to the length of the oxidation period. Beyond 130–150°C most of the activation disappeared. No production of CO could be observed in this temperature range. Figure 3a shows that curves 1–3 envelop themselves at low temperatures whereas curve 4 displays a delayed start. This tendency increases for even longer exposures (see curves 5 and 6, Fig. 3b).

Another way of strengthening the oxidation treatment obviously consists of carrying it out at increasing temperatures. The same experimental procedure used in the preceding runs was applied (flowing air, 1 h, various temperatures). No activation resulted from exposure to air at room temperature. Slight activation resulted from oxidation at 200°C and its effect was four to five times smaller than that observed after oxidation at 300°C. Figure 4 shows the results of oxidation conducted in the temperature range 300–500°C. It can be seen that the temperatures of the maximum rates increased from 62 to 110°C with increasing strength of oxidation. Curves 1–3 in Fig. 4a envelop themselves in the low temperature range whereas curves 3–5 in Fig. 4b, corresponding to stronger oxidations, display the same arrangement as curves 4–6 in Fig. 3b.

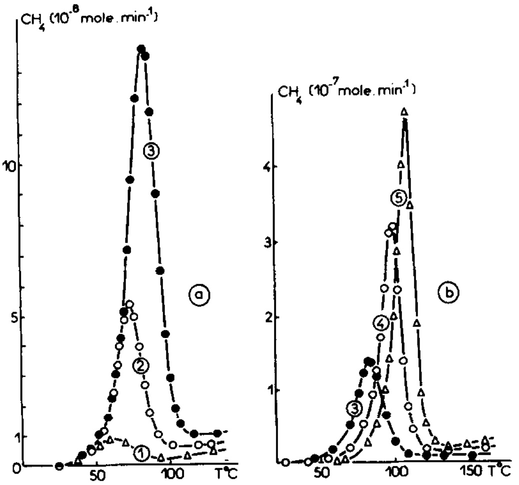

FIG. 4. Influence of the temperature of preoxidation by air for 1 h upon the variation of the resulting methanation activity as a function of temperature: 300°C (curve 1), 350°C (curve 2), 400°C (curve 3), 450°C (curve 4), 500°C (curve 5). Rate of heating: 6 K min^{-1}.

Another way of revealing the effect of preoxidation consists of monitoring the time variation of the resulting rate at a constant temperature. This procedure made the transient character of the effect under study appear clearly. After a standard preoxidation (1 h, 400°C) the catalyst was cooled to the desired temperature. At 50°C, the rate increased for nearly 40 min to 1.5×10^{-8} CH_4 min^{-1} and then decreased for 3 to 4 h to nearly one-tenth of its maximum value. The same kind of evolution was observed at 85°C but required a much shorter time period (about 15 min) for its completion (maximum rate obtained: 3.8×10^{-8} CH_4 min^{-1}). At 125°C the rate started from its maximum as soon as the metal was brought into contact with the reactant mixture and the activity disappeared within a few minutes.

There was no need to use air to activate the catalyst, as can be seen in Fig. 5, the results of which were obtained with He + 30 ppm O_2 as a pretreatment gas. An advantage of using diluted O_2 as an oxidizing agent is that the O_2 meter could be used to monitor O_2 consumption. Table 1 gives the amount of O_2 reacted with Rh during different oxidations. This amount has been converted into the corresponding number of layers of oxide assumed to be Rh_2O_3 and uniformly spread over the powder surface.

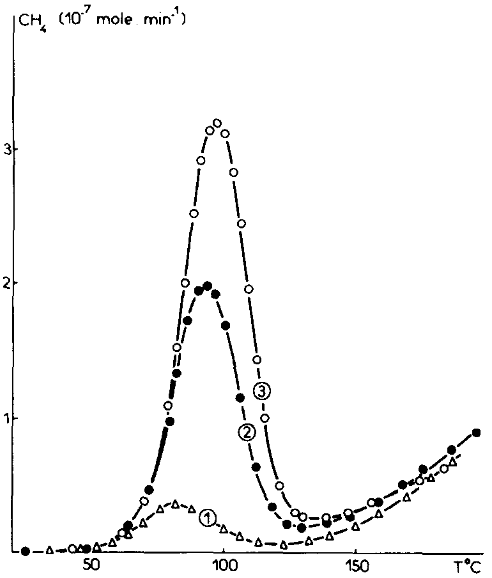

FIG. 5. Influence of the time of preoxidation by He + 30 ppm O_2 at 400°C upon the variation of the resulting methanation activity as a function of temperature: 5 h (curve 1), 15 h (curve 2), 40 h (curve 3). Rate of heating: 6 K min^{-1}.

The shortest treatment (1 h) did not induce any visible activity. The next three treatments (5, 15, and 40 h) resulted in curves 1, 2, and 3 of Fig. 5 which display increasing activation as a function of increasing oxidation but no delayed start of reaction during the temperature ramp.

When, instead of being cooled under helium after the oxidizing treatment, the catalyst was fed H_2 at the pretreatment temperature for about 10 min before being cooled under H_2, no activation was observed. The same was true when the preoxidized powder was heated under H_2 from room temperature to about 150°C before being cooled and fed the reactant mixture in the low temperature range.

Simultaneous Occurrence of the Catalytic Activation of Rh and Its Reduction after Preoxidation

(*a*) *Case of the powder.* Reduction of the oxidized Rh layers was expected to start even at a moderate temperature if the layers were brought into contact with H_2 or the reactant mixture. As both activation of the powder and reduction of the preoxidized layers are transient phenomena, the question of their more or less complete simultaneity naturally arose.

After subjection of the catalyst to the standard pretreatment (air, 1 h, 400°C), the water production under pure H_2 was looked for at room temperature by the use of an electrolytic hygrometer. The reading of the latter immediately went out of its measurement range (1000 ppm) and the meter had to be bypassed. An hour later the water content of H_2 at the reactor outlet did not exceed a few tens of ppm and could thus be monitored continuously. The temperature was then programmed to increase at a constant rate of 6 K min^{-1}. The rate of production of water increased accordingly and passed through a maximum at about 90°C.

The same pretreatment and subsequent procedure were applied to the catalyst except for substitution of the reactant mixture (H_2 + CO_2) with pure H_2. The same observations could be made at room temperature. Thus, after pretreatment, the powder was flushed with H_2 for 1 h while the hygrometer was bypassed. Afterward the reactant mixture was substituted for H_2 and directed toward the hygrometer at the reactor outlet. The temperature was then programmed to increase at the same rate as previously. Figure 6 shows the variation in the rates of production of H_2O and CH_4 as a function of temperature. The curve for methane production closely resembles those in Fig. 2. The curve for water produc-

TABLE 1

Amount of O_2 Reacted during Preoxidation Conducted at 400°C with He + 30 ppm O_2 and for Increasing Lengths of Time

	Time (hr)			
	1	5	15	40
O_2 reacted (10^{-5} mole)	1.0	2.9	6.9	15
Number of oxide layers	1.6	4.5	10.7	23.3

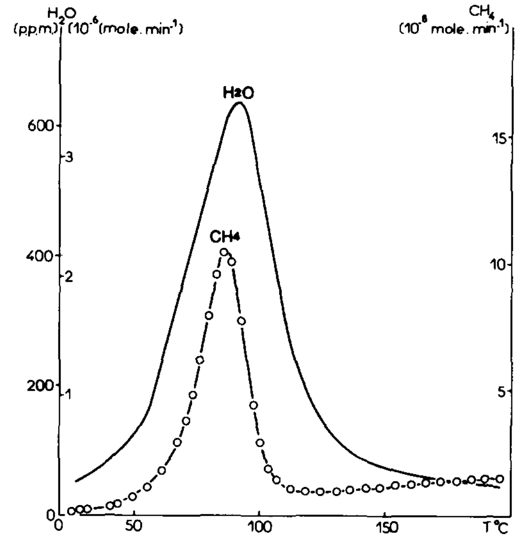

FIG. 6. Variations in the rates of CH_4 and H_2O production versus temperature after preoxidation by air for 1 h at 400°C. Cooling under air preceded feeding of the reactor with H_2 for 1 h at room temperature. The reactant mixture (H_2 + 5% CO_2) was then substituted for H_2 and the temperature was increased at 6 K min^{-1}.

tion is quite similar to that obtained with pure H_2 as the water production due to the methanation reaction is very small relative to the water production due to the reduction of preoxidized powder (less than 6% at 85°C, temperature of CH_4 maximum). The parallelism between both variations is even more striking when the time of response of the hygrometer is taken into account.

(*b*) *Case of the ribbon.* In our previous contributions (*4, 22*) concerning the Rh ribbon we had not tried to obtain evidence for the reduction of the oxide layer by direct detection of the water produced. For the sake of comparison it was appropriate to do this experiment. The same Rh ribbon used in the previous work was employed. As previously reported, no activity was displayed by the catalyst following prolonged exposure (15 h) to pure H_2 at 400°C. The metal was then subjected to a typical pretreatment which consisted of a feed with a flow of He + 30 ppm O_2 at 400°C for 1 h. After the catalyst was cooled under He at room temperature, the reactant mixture (H_2 + 5% CO_2) was substituted for He and the temperature was made to increase at a constant rate of 6 K min^{-1}. Curve 1 in Fig. 7 shows the resulting rate of production of CH_4 as a function of temperature after He–O_2 pretreatment and closely resembles those previously reported (*22*). Curve 2 shows that CO was also produced and that it was the main carbonaceous product of reaction. For instance, when CH_4 reached its maximum rate of production, CO was produced at a rate nearly 10 times greater. CO attained its maximum production at a temperature about 100°C higher than that corresponding to the CH_4 maximum and was then produced more than 40 times faster than CH_4 (less then 3% conversion of CO_2). It can be seen, however, that the rate of CO production ceased to increase exponentially beyond the temperature corresponding roughly to the maximum of CH_4. A thermal increase of 100 K increased the rate by a factor lower than 2.

After deactivation of the catalyst was completed under prolonged exposure to H_2 at 400°C, the same oxidizing pretreatment

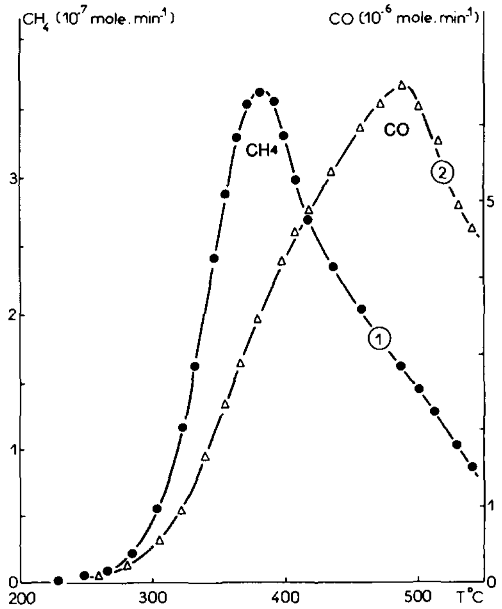

FIG. 7. Comparative case of Rh ribbon: rates of CO and CH_4 production versus temperature during linear heating (6 K min^{-1}) of the catalyst after pretreatment with He + 30 ppm O_2 at 400°C for 1 h.

was applied once more. After being cooled to room temperature, the catalyst was fed *pure* H_2 whereas the temperature was increased in the same manner as in the preceding experiment. The gas leaving the reactor was directed toward the hygrometer in an attempt to detect the reduction of the oxide film which was formed on the Rh surface during pretreatment. Figure 8 displays the water content of the exit gas as a function of temperature. One can see that part of the film was reduced at low temperatures (<200°C) but that the major amount of water was produced beyond 300°C with a maximum reduction rate at about 325°C. Clearly it appears that the oxidized Rh ribbon was much less easily reduced than the powder. However, a meaningful common feature is that the activation closely relates to the reduction of the oxidized layers as the CH_4 and H_2O production peaks remained linked in both cases.

Behavior of the Preoxidized Powder at Temperatures Lying between 120 and 300°C

Apart from the activation effect imparted by the preoxidation to the Rh powder and appearing between approximately 50 and 100 or 120°C, there exists another consequence which appeared at higher temperatures, roughly between 150 and 300°C. The intrinsic activity of rhodium, that is to say, the activity displayed when no preoxidation was carried out, became visible at about 140°C (Fig. 2, curve 1). After preoxidation and when the temperature increased beyond approximately 120°C during the program of heating, the extra activity possessed by the metal became more time resistant and even began to increase slowly until the intrinsic activity became evident (Fig. 2, curve 2). Nevertheless, the rate variation was such that the activity of the preoxidized powder became lower than the intrinsic activity at temperatures higher than 180°C. Both curves tended to become identical beyond 350°C. When the catalyst was cooled after the experiment and subjected to a second program of heating, no extra activity could be observed and curve 1 was obtained.

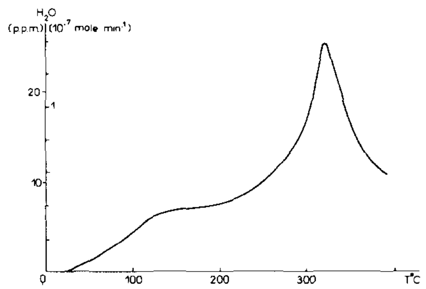

FIG. 8. Comparative case of Rh ribbon: water content in H_2 flow at the reactor exit versus temperature during linear heating (6 K min^{-1}) of the catalyst. Same pretreatment as for Fig. 7.

Hydrogenation of CO_2 Preadsorbed in the Presence of H_2

Another way of revealing the effect of preoxidation of rhodium upon its catalytic behavior consists of attempting to observe this effect upon separate parts of the reaction instead of the whole process. To this end the metal was placed in a situation of adsorbing CO_2 in the presence of H_2 but without being able to make it react into CH_4.

(*a*) *Preadsorption on the reduced metal.* The powder was maintained under a flow of pure H_2 at 400°C overnight and then cooled to room temperature still under H_2. The reactant mixture (95% H_2 + 5% CO_2) was then made to flow through the reactor for 3 h at 25°C. No methane production was found but a small amount of water was produced. The catalyst was then flushed with pure H_2 whereas the temperature was raised at a constant rate (6 K min^{-1}) and the desorbed products were monitored using chromatographic and hygrometric analyses.

Neither CO nor CO_2 was desorbed. Curve 1 of Fig. 9 shows the CH_4 peak which was produced with a maximum at about 245°C. Curve 1 of Fig. 10 shows the corresponding peak of water. The slight delay of the H_2O peak with respect to that of

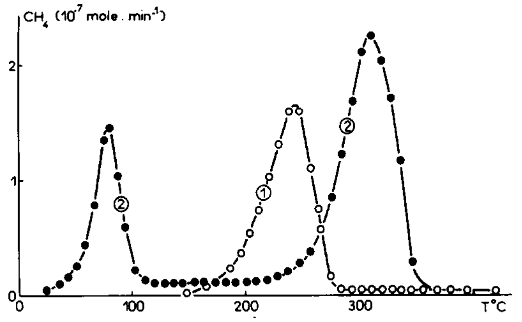

FIG. 9. Production of CH_4 during the temperature-programmed reaction of H_2 with CO_2 preadsorbed in the presence of H_2 (95% H_2, 5% CO_2) on catalyst preoxidized (curve 2) or not (curve 1). Temperature of preadsorption: 25°C. Length of preadsorption: 3 h. Rate of heating: 6 K min^{-1}.

CH_4 must be ascribed to the response time of the hygrometer (about 3 min). The ratio of the total amount of H_2O to that of CH_4 (0.73) is close enough to unity (taking into account some irreducible uncertainty concerning the water analysis) to support the assumption that most of the chemisorbed species was in the form of CO and was reacted into CH_4 and H_2O. The assumption that some CO_2 could have dissociated into C_{ads} as well as CO_{ads} on chemisorption at 25°C cannot be rebutted and experimental evidence for this assumption when the chemisorption occurred, for instance, at 100°C, will be given later. The second oxygen atom of CO_2 must have reacted with H_2 at room temperature during chemisorption. This result agrees with those obtained by Falconer and Zăgli in the case of a nickel/silica (*27*) or a ruthenium/silica catalyst (*28*).

(*b*) *Preadsorption on the preoxidized metal.* A similar experiment was carried out on the powder after it had been preoxidized in the standard manner. Cooling of the powder to 25°C was effected under flowing air. After a short He flush, the reactant mixture was admitted. From this time onward, the experiment was performed exactly as described in the previous section. Curves 2 (or 2′) of Figs. 9 and 10 show the respective rates of CH_4 and H_2O production versus temperature. Each curve displays two peaks. The first peaks correspond obviously to those of Fig. 6. In particular almost all of the water (94%) originated in the completion of the catalyst reduction. The second CH_4 and H_2O peaks

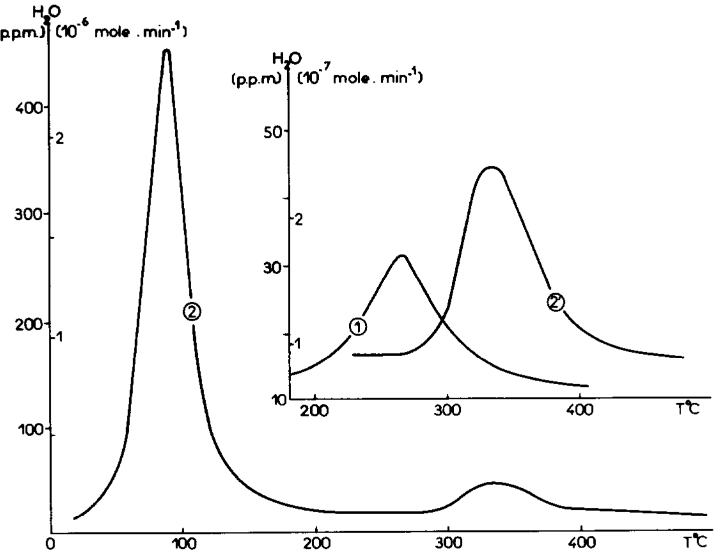

FIG. 10. Production of H_2O during the temperature-programmed reaction of H_2 with CO_2 preadsorbed in the presence of H_2 (95% H_2, 5% CO_2) on catalyst preoxidized (curve 2 and 2′) or not (curve 1). Temperature of preadsorption: 25°C. Length of preadsorption: 3 h. Rate of heating: 6 K min^{-1}. Curve 2′ is the magnification (× 6.25) of the second peak of curve 2.

can reasonably be conceived as having the same meaning as the corresponding peaks of curves 1 of Figs. 9 and 10 except for the fact that they result from hydrogenation of CO adsorbed on a surface which had been oxidized prior to the experiment. One can observe that a greater amount of CO_2 was adsorbed in the case of preoxidation (about 2.3 more). Part of this greater amount is much more reactive and the remaining part much less reactive than that adsorbed on the reduced surface.

To determine whether the mere presence of oxygen on the preoxidized surface was responsible for the modifications observed in the adsorption of CO_2, the latter was conducted under conditions such that no simultaneous reduction could happen. To this end, the oxidized powder was flushed at room temperature with the mixture (He–5% CO_2) instead of H_2–5% CO_2 for an equal time, after which pure H_2 was admitted to the catalyst and the temperature was increased in the same way as in the preceding runs. No methane could be found even at the lowest visible level. On the contrary, when the preoxidized metal was partially reduced by a 2-h flush with pure H_2 at room temperature prior to exposure to He–5% CO_2, nearly the same H_2O and CH_4 production rates as on curves 2 of Figs. 9 and 10 resulted.

DISCUSSION

The main conclusion of this work is that strong activations, albeit transient ones, can result from preoxidation of powdered Rh as was the case for Rh ribbon. Catalytic activity is manifested in a temperature range in which no activity at all would be observed if the metal were not preoxidized. Despite the smallness of the rates measured, the level of activation which can be reached is very high, since the intrinsic activity of the sample extrapolated to such temperatures (50–100°C) would be four or five orders of magnitude lower and would therefore escape any attempt at measurement.

In the case of the ribbon, direct examination of the metal by Auger electron spectroscopy showed that its surface had been cleaned efficiently and had remained in this state after prolonged exposure to H_2 at 400°C (*4*). In the present work we had no facility with which to obtain such direct evidence for the powder. What can be said, however, is that the powder was of higher initial purity than the ribbon and that it was subjected to the same cleaning procedures expected to be more efficient due to the morphology. Moreover, the surface area deduced from CO chemisorption (*26*) was in good agreement with the BET area determined by Kr physisorption.

The possibility for activation to be viewed in terms of contamination and decontamination effects must nevertheless be examined more thoroughly. In agreement with this view the lack of activity of the powder in the low temperature region ($T <$ 100°C), although not surprising, would result from a severe surface contamination which a proper O_2 treatment would transiently remove. An increase in activation following oxidations of increasing severity would then be observed because of more and more complete cleaning of the surface. However, oxidation of deeper layers of the sample occurs at the same time. As a high level of water production was observed when the oxidized sample was submitted to H_2 at room temperature, one must reasonably assume that the top oxide layer was easily reduced and that subsequent reduction was slackened due to diffusion. The catalytic activity which was observed when the powder was heated (Figs. 3–5) would therefore have to be ascribed to the clean and reduced part of the Rh surface, the extent of which would be an increasing function of the strength of preoxidation. A given level of CO_2 hydrogenation would have then been attained at lower temperatures after stronger oxidations, in contrast to what can be seen in Figs. 3a, 4a, and 5 where the curves envelop themselves at their beginning. This fact clearly suggests that the same and therefore complete cleaning had been achieved after every preoxidation, which resulted in the same initial increase in activity.

That the maximum level of activity eventually obtained increased with the strength of oxidation might be viewed as a higher poison resistance imparted to the metal by a deeper oxide layer. It is unlikely that contaminants could be oxidized at such low temperatures. Furthermore, the origin of possible contaminants would have to be looked for either in a segregation effect or in insufficient purification of the gases.

Segregation effects can hardly be imagined at such low temperatures especially if one makes reference to what should be the rate of diffusion to explain so fast a deactivation. A still much faster segregation should moreover have occurred during the pretreatment effected at higher temperatures and would have resulted in very easy and complete cleaning of the sample. Consequently the phenomena studied would have progressively disappeared and steady activities would have been observed below 100°C. Nothing like that happened even after a long period of working of the catalyst and the extent of activation following a given pretreatment remained constant.

If we now turn our attention toward contamination by gases, impurities would have to be suspected in H_2 as the deactivation proceeded both under H_2 and under the reactant mixture. Due to the mode of purification of H_2 the only contaminant which could reasonably be suspected consisted of traces of air due to irreducible leaks at Swagelock connections or valves. The resulting O_2 level was, at any rate, below our limit of detection (0.1 ppm). Moreover, addition of O_2 was shown to exert no effect in the temperature range involved.

Another kind of interpretation to which reference is sometimes made (*6*, *10–12*, *16–18*) is a possible promoting effect resulting from the presence of some chemisorbed oxygen on the metal surface or in its near-surface region. Some optimum oxygen coverage would be expected for an optimum effect to be induced since a completely covered surface would be inhibited. This would explain why during isothermal reductions the rate first increased and displayed a maximum as a function of time. In the same manner the increasingly difficult start of reaction exhibited by the curves in Figs. 3b and 4b after oxidations of increasing severity might be viewed as the result of an increasing oxygen excess on the surface. In fact this effect had a different origin and the more difficult start of reaction was only the consequence of a less easy reduction of the oxide layer when the latter was built up under air at the highest temperatures (Fig. 3b) or during the longest exposures (Fig. 4b).

Figures 3a, 4a, and 5 permit a better discussion of the possible improvement of catalytic activity due to the presence of oxygen on the surface. Initial coincidence of the curves is well understood if it is realized that, at the end of a pretreatment, a given time of reduction cannot discriminate between different oxide layers resulting from oxidations of increasing strength inasmuch as the amount of oxide reduced during this time is small compared to the total initial amount of oxide. When depletion of the oxide layer is no more negligible the curves separate from one another. This condition was fulfilled within a time period shorter than that required to obtain the optimum activity versus time in isothermal experiments carried out at temperatures roughly equal to those at which curves 1, 2, and 3 of Fig. 3a, curves 1 and 2 of Fig. 4a, and curves 1, 2, and 3 of Fig. 5 separated from one another. Separation of the curves occurred therefore within the period during which an excess of oxygen on the surface would be suspected to exert a negative effect upon the activity according to the interpretation considered. If such had been the case, however, the curves should have displayed the reverse order as the stronger the initial oxidation the higher the remaining oxygen content at any given time of reduction. It can be concluded that, as in the case of massive Rh, there is a failure of this kind of assumption in interpreting the activation in a detailed manner.

Clearly the extra activity induced by preoxidation of the metal appears to be a property of the freshly reduced surface. The link between activation and production of a fresh surface appeared strong enough to make the activation parallel reduction of the preoxidized surface layers even when the morphology change made the reduction occur in a range of much lower temperatures. The possibility for surface atoms of metallic catalysts to be dislodged by successive oxidations and reductions has been repeatedly reported and we previously showed its occurrence in the case of a Rh ribbon (*4*). Facetting and roughening of the surface are macroscopic consequences of a surface mobility which must obviously occur first at the atomic level. One can easily assume that active, though unstable, configurations may appear under these conditions so that the high activity would be a property of the disordered state of the nascent surface. Deactivation would then result from thermal restructuring of the surface. Most of the facts reported here and, in particular, the point just discussed in the preceding paragraph, can readily be explained on a qualitative basis in agreement with this view. Although oxide films formed on solid and powdered Rh are of strikingly different reducibility, disordering of the surface should occur with equal probability as the driving force (reduction of the oxide) is the same in both cases and in both cases transient reduction of the oxide generated transient catalytic activity. This was all the more striking in the case of the powder as the temperature was well below that required for obtaining the same activity but in the steady state.

Not only can more active catalytic centers be assumed to exist on a nascent surface but one can also easily imagine that other parts of the surface should be able to react more energetically with the reaction partners. Stronger binding can result in lower catalytic activity. That the surface properties can be modified according to these two opposite directions seems indeed to be the case if one considers the results displayed in Figs. 9 and 10. When CO_2 can adsorb onto the nascent surface, a part of the adsorbate finds itself involved on more active catalytic centers, whereas the remaining part is bound more firmly on other and more energetic chemisorption sites as the resulting thermoreacted CH_4 peak is produced at higher temperatures than with the non-pretreated metal. This observation appears consistent with the depressed activity which is exhibited between roughly 180 and 300°C on the pretreated surface (Fig. 2, curve 2). What is most surprising is that the CH_4 peak obtained under the same conditions on the non-pretreated metal disappears, so that no part of the corresponding surface seems to remain. In its nascent state most of the surface is therefore modified in its reactive behavior. However, only on part of the surface does this modification result in a remarkable though transient catalytic activation.

From a kinetic point of view a meaningful difference seems to lie in the fact that no CO was produced when the transient activity was induced on the powder whereas it was the main product on the solid sample. This was the result not of some intrinsic difference between the two samples but, as we shall report later in a mechanistic study, of the ability of CO to be reacted into CH_4 when the active area is large enough (*26*).

A natural question would concern the nature of the elementary steps of the reaction which are sensitive to the activation. It has been shown that, once oxidized, the surface is able to adsorb more CO_2 but this is a minor effect. Figures 9 and 10 clearly show that, once chemisorbed, CO_2 is able to be much more readily hydrogenated on the activated surface. We will later provide experimental data supporting the view that the active surface should cause faster breaking of the C–O bond.

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