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Complex Influence of Carbonaceous Residues on the Catalytic Activity of Rhodium in C_2H_4 Hydrogenation

ANNIE AMARIGLIO AND HENRI AMARIGLIO

Laboratoire Maurice Letort (C.N.R.S.), Route de Vandoeuvre, Boîte Postale No. 104, 54600 Villers-lès-Nancy, France, and Université de Nancy 1, Boulevard des Aiguillettes, Boîte Postale 239, 54506 Vandoeuvre-lès-Nancy, France

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The complex effect of carbonaceous residues upon the catalytic activity of massive Rh in C_2H_4 hydrogenation and its interference with the metal activation by oxidation–reduction processes have been illustrated. The variation of the catalyst activity as a function of time on stream has been monitored either by feeding the catalyst with the complete reactant mixture (95% H_2, 5% C_2H_4, 18 ppm O_2) in a permanent way or by feeding it with oxygen-doped hydrogen (H_2–18 ppm O_2) only and periodically probing the activity for a short time. In the second case no contamination of the surface had to be invoked to account for the catalyst behavior. In the first case there is initial inhibition by carbonaceous residues, but a progressive increase of activity followed. The final steady rate was unexpectedly higher than in the second case. This complex behavior has been explained as resulting from an interference of the initially rapid inhibition with the underlying continuous activation of the surface by the H_2–O_2 reaction.

INTRODUCTION

We have previously reported on the high promoting influence that O_2 traces can exert on C_2H_4 hydrogenation either when O_2 is contained in the reactant mixture (*1*) or when it has first been incorporated into the Rh lattice and then back-diffuses to the surface during reaction (*2*).

The O_2 activating effect might be regarded as resulting from a cleaning of the surface by oxidation and gasification of impurities or from the improvement of the surface catalytic properties due to the presence of O atoms on the surface or in the near-surface region (*3, 4*).

We have described (*1, 2*) several experiments which showed that, at least in the present case, the main cause of the O_2 activating effect had to be found on another ground. We have proposed to explain the effect as the result of the structural sensitiveness of the metal lattice to the H_2–O_2 reaction. It is a well-known fact that the latter reaction is able to bring about gross rearrangements of the catalyst surface (*5–8*). While the surface is being rearranged metal atoms are dislodged and special atomic configurations may reasonably be assumed to be formed. All of the experimental observations can be unraveled if one assumes, on the one hand, that some of those configurations are especially efficient in C_2H_4 hydrogenation and, on the other hand, that their lifetime is limited due to the spontaneous thermal restructuring of the surface.

In a recent contribution (*9*) we have reported on an additional behavior of the system which would be hard to explain according to usual views. It consisted in the kinetic response of the Rh sample catalyzing the H_2–O_2 reaction when C_2H_4 was suddenly added to the reactant mixture. An immediate inhibition occurred which was progressively compensated by a slow self-reactivation of the catalyst. We have proposed to account for this unexpected behavior by assuming that the thermal restructuring of the surface can be impeded by carbonaceous residues. The mobility of extra-lattice atoms should in effect be de-

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creased by the carbonaceous residues bound to them. Another possibility would be that the crystallographic locations which the dislodged atoms tend to occupy preferentially might be partly filled up with carbonaceous species. Longer lifetimes of the moving units would therefore result.

Now, if one takes into account the complex character of the hydrocarbon action upon the catalyst, it appears in order to revert to some of the experiments reported in Ref. (*1*). In some of them in effect the catalyst was fed with a flow of H_2 with a small content of O_2. The variation of its catalytic activity in C_2H_4 hydrogenation as a function of time was monitored by periodically contacting it with the reactant mixture *for 30 sec only*. That procedure allowed us to keep the metal free of hydrocarbon contamination to the best feasible extent. Due to the complex action of C_2H_4 molecules upon the catalyst it is now necessary to look for the modifications which the *continuous* feed of the catalyst by the complete reactant mixture might originate.

EXPERIMENTAL

Catalyst. A rhodium ribbon of the same kind as those previously used (*1, 2*) was chosen (Heraeus; 99.99% purity). The cleaning procedure was the same as formerly and its efficiency was demonstrated in a similar way (examination of the sample by Auger electron spectroscopy).

Kinetic measurements. The kinetic determinations were performed in a flow-type apparatus which has been previously described (*2*) with no further modification.

Auger electron spectroscopy. The same equipment as previously (*2*) was used for AES examinations. Its particular relevance to catalytic studies comes from the possibility that quick transfers of the sample can be effected from the preparation chamber into the analysis chamber.

RESULTS

The first experiments are illustrated in Fig. 1. They constitute extensions of previous ones (Ref. (*1*), Section 8a) which were intended to discover whether O_2 activates the catalyst only by itself or through its reaction with H_2. To that end, the catalyst first deactivated by a suitable exposure to pure H_2 (15 hr, 300°C) was exposed to various gaseous environments.

Curves 1 and 2 are the same as curves 1 and 2 of Fig. 12 in (*1*). Curve 1 had been obtained when the deactivated catalyst had been fed with (He–18 ppm O_2) first and then with (H_2–18 ppm O_2). Under the latter exposure the catalytic activity had been monitored by a periodical feed with the reactant mixture (95% H_2, 5% C_2H_4, 18 ppm O_2) for 30 sec only. Curve 2 gives the catalyst behavior when no oxidizing treatment with He–O_2 had been applied before admitting H_2–O_2.

If the catalyst was deactivated first and then exposed to the complete reactant mixture in a *continuous* way, curve 3 resulted instead of curve 2. The activity began to rise as under the H_2–O_2 mixture but passed through a maximum and a minimum value successively before increasing again, though in a slower fashion. After 20 hr of continuous feed the steady state was not attained, in contrast with curves 1 and 2. The activity continued to increase beyond the stationary level of the preceding curves in spite of the fact that no protection of the surface from the hydrocarbon contamination could operate under those conditions. The final steady state was attained after nearly 50 hr and was the same as that corresponding to curve 2 of Fig. 3 and to curve 3′ of Fig. 4.

It appears quite sensible to suppose that the break which occurred during the initial increase of activity stemmed from an inhibition effect due to the continuous presence of C_2H_4. In order to check that point the hydrocarbon feed was removed and re-established from time to time. The result is displayed in Fig. 2. Cutting off C_2H_4 resulted in a quick reincrease of activity whereas reintroducing it made the activity

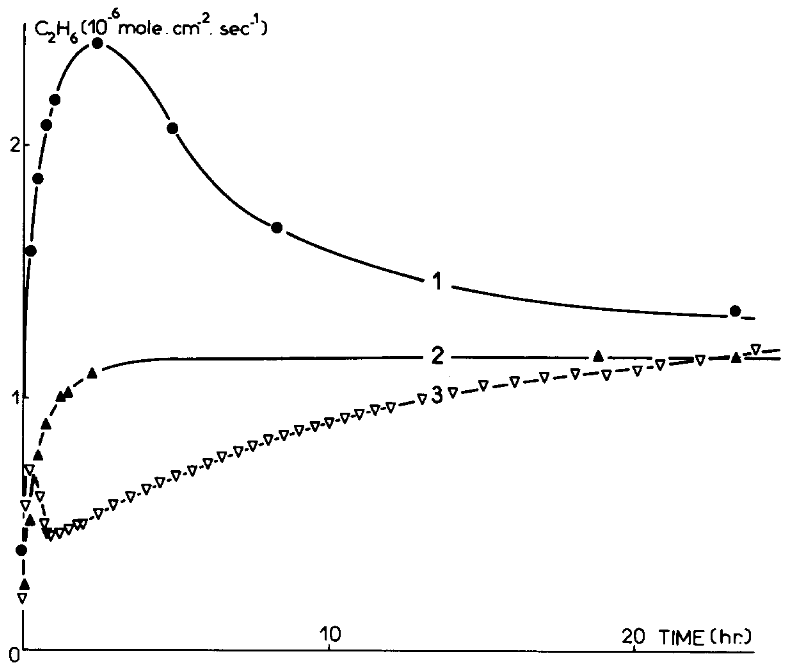

FIG. 1. Variation of the rate of C_2H_4 hydrogenation at 205°C as a function of time. Curve 1. Pretreatments: (a) 15 hr in a flow of pure H_2 at 300°C; decrease of temperature down to 205°C in a flow of H_2; (b) 22 hr in a flow of He–18 ppm O_2 at 205°C; (c) 3 min in a flow of pure He at 205°C. Measurements: The catalyst is then maintained in a flow of H_2–18 ppm O_2 and its activity is monitored by flushing it with the reactant mixture (95% H_2, 5% C_2H_4, 18 ppm O_2) for 30 sec from time to time. Curve 2. Pretreatment: the same as (a) for curve 1. Measurements: they follow (a) immediately and are done in the same manner. Curve 3. Pretreatment: the same as (a) for curve 1. Measurements are done under the *continuous* flow of the complete reactant mixture.

fall off again. The repetition of the experiment shows that every exposure of Rh to the gas free from C_2H_4 made the activity increase to what it would have equalled approximately if C_2H_4 had been absent from the start.

That the hydrocarbon exerts an inhibition effect is thus shown unequivocally. Nevertheless, the presence of C_2H_4 compels the activation of the catalyst to reach a higher level. In order to test this conclusion in another way the procedure giving rise to curve 1 (Fig. 1) was repeated. After the variation of activity had been monitored periodically for nearly 30 hr the continuous feed of the catalyst with the reactant mixture was established. After an initial but limited inhibition a distinct increase of activity was observed in C_2H_4 hydrogenation (curve 2; Fig. 3). It can therefore be stated that the final level of activity is much higher when the catalyst is contacted by the hydrocarbon continuously. Curve 3 of Fig. 3 shows the response of the catalyst when O_2 was removed from the reactant mixture. As a part of the active surface was covered by oxygen an increase of activity was immediately observed. The usual deactivation took place soon after as the surface ceased to be activated by the H_2–O_2 reaction (*1*).

Other experiments have been conducted in order to demonstrate that different kinds of transients can be displayed according to the treatments to which the catalyst is subjected prior to its permanent feed with the complete reactant mixture. To make the comparison easier curve 3 of Fig. 1 has been reproduced in Fig. 4 (curve 1). It illus-

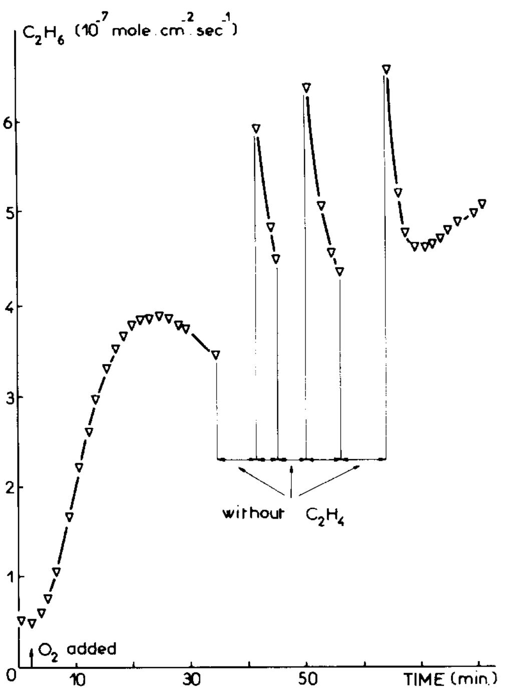

FIG. 2. Variation of the rate of C_2H_4 hydrogenation at 205°C as a function of time. Pretreatment: the same as (a) of curve 1, Fig. 1. Measurements are done under *continuous* feed of reactant mixture (95% H_2, 5% C_2H_4, 18 ppm O_2) except for the periods without C_2H_4 during which the catalyst is maintained under H_2–18 ppm O_2.

trates the catalyst behavior when no activating pretreatment separated the initial deactivation under H_2 from the permanent feed of the catalyst with the complete reactant mixture.

Curve 2 of the same figure shows what happened when the catalyst, first deactivated under H_2, was flushed with He–O_2 for 2 hr before being fed with the complete reactant mixture. Higher activities were displayed initially in the latter case just as in Fig. 1 for curve 1 with respect to curve 2. The subsequent behavior is essentially similar to that of curve 1.

In addition to the oxidizing treatment by He–O_2 the catalyst may be flushed with oxygen-containing hydrogen (H_2–18 ppm O_2) before being fed continuously with the complete reactant mixture. Curve 3 was obtained in this way. No increase of activity could be seen in the initial period. The activity decreased rapidly for about 1 hr before increasing slowly. The eventual steady state still corresponded to a higher level of activity than that of curve 1 of Fig. 1 and was the same as that of curve 2 of Fig. 3.

DISCUSSION

The experiments show clearly that the hydrocarbon exerts an inhibition upon the catalyst. This is entirely in agreement with current views concerning the building-up of carbonaceous deposits upon the surface of catalysts (*10*). As that poisoning of the surface is an irreversible process one would have expected that the variation of the catalytic activity on curve 3 of Fig. 1 (or curve 1, Fig. 4) should have consisted of a decrease of the rate of C_2H_4 hydrogenation down to a negligible value with respect to the maximum rate reached during the beginning of the reduction of the preoxidized surface.

If such is not the case we must consider first that the coverage by carbonaceous residues remains limited. The same conclusion has already been drawn from direct observations of the surface by Auger spectroscopy after it had been contacted by the reactant mixture (*1*). The reason why the carbonaceous deposit remains limited on the surface comes most likely from the fact that it can be reacted by H_2 into CH_4 as the main product. In fact very small amounts of CH_4 were always produced for times of about 10 min when the catalyst was flushed with *pure* H_2 just after it had been continuously fed with the complete reactant mixture. Some limited reincrease of activity resulted. In addition we cannot exclude that the O_2 traces contained in H_2 even when C_2H_4 was removed could burn off a part of the residues. Unfortunately we had no means to detect traces of carbon oxides.

However that may be, Fig. 2 clearly displays that there is a limited and reversible inhibition by C_2H_4.

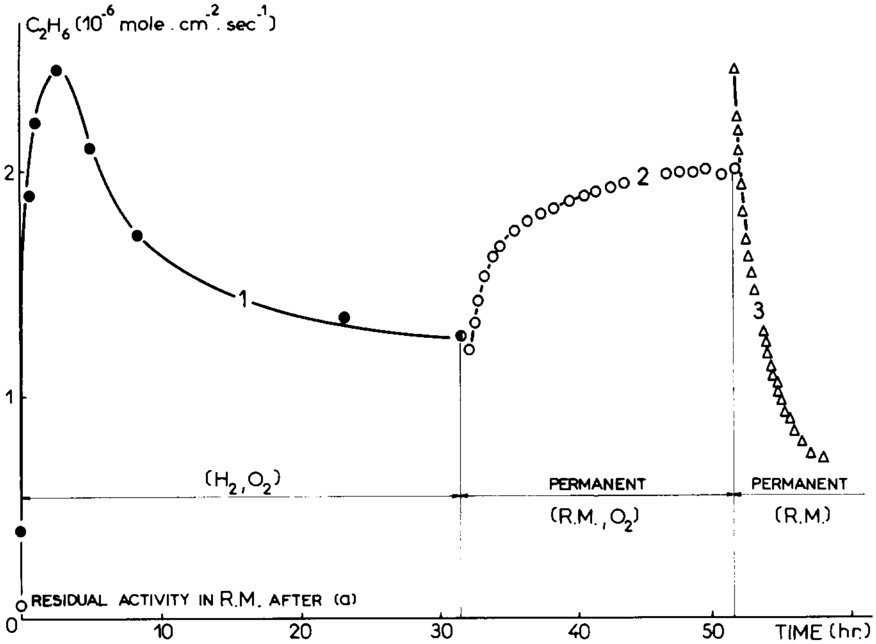

FIG. 3. Variation of the rate of C_2H_4 hydrogenation as a function of time. Curve 1: the same as curve 1 of Fig. 1. Curve 2: rate variation corresponding to the permanent feed with the complete reactant mixture. Curve 3: rate variation under permanent feed when O_2 is removed.

The formation of the active surface can interfere with its contamination by the hydrocarbon in different ways according to the procedure applied. This is demonstrated by Fig. 4. Higher initial activities are displayed on curve 2 with respect to curve 1 just as in Fig. 1 for curve 1 compared to curve 2. The maximum of curve 2 (Fig. 4) was attained sooner than that of curve 1 (Fig. 1) not only because the oxidizing pretreatment had been shorter but also because of the hydrocarbon poisoning.

Attention must be paid to the fact that the maximum which occurs on curve 1 (Fig. 4) originates in the surface contamination by C_2H_4 interfering with the catalyst activation by the H_2–O_2 reaction. No maximum would happen if the activity was monitored by discontinuous probings (see curve 2, Fig. 1). On the contrary, curve 2 (Fig. 4) would exhibit a maximum even if the rate of reaction was measured in the discontinuous way (see curve 1, Fig. 1). In that case a good part of the catalyst activation results from the reaction of the preincorporated O_2 back-diffusing to the surface and being taken away by H_2 (*1*, *2*). Even in the absence of permanent C_2H_4 a maximum occurs because of the depletion of the near-surface region. A complementary cause of catalyst activation arises from the reaction involving gaseous O_2. When the rate of reaction is measured under continuous feed of the catalyst with the complete reactant mixture the contamination of the surface by carbonaceous residues interferes with the latter phenomena and the period of decreasing activity has a dual origin.

Curve 3 displays no initial rising part because the complete reactant mixture contacted the catalyst only when the maximum which might have been revealed by periodical probings had already occurred.

However, the surface events which control the catalytic activity cannot be reduced to the mere addition of the processes considered so far. If this had been the case one would not have observed such a discrepancy in the times required for the steady states to be reached according to the con-

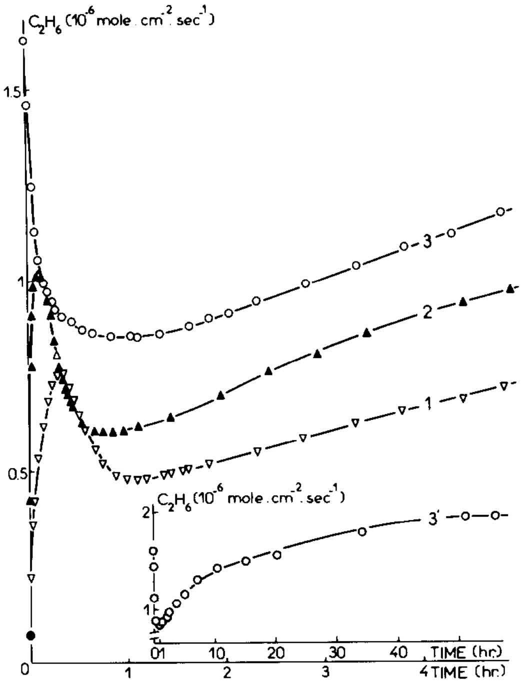

FIG. 4. Variation of the rate of reaction at 205°C as a function of time. Curve 1. the same as curve 3, Fig. 1. Curve 2. Pretreatments: the same as (a) curve 1, Fig. 1 followed by an exposure for 2 hr to a flow of He–18 ppm O_2. Measurements: same conditions as for curve 1. Curve 3. Pretreatments: the same as (a) curve 1, Fig. 1 followed by two successive exposures to flows of He–18 ppm O_2 for 4 hr and of H_2–18 ppm O_2 for 1 hr. Measurements: same conditions as for curve 1.

tinuous or discontinuous feed of the catalyst with C_2H_4 (curves 2 and 3, Fig. 1; curve 3′, Fig. 4). Moreover, the steady state corresponding to the complete and permanent reactant mixture would have been expected to establish itself at the end of periods of decreasing activities and to correspond to a lower activity than that of curve 2 in Fig. 1. Another surface process must be invoked in order to account for the occurrence of a minimum and the subsequent slow reincrease of activity which is displayed in every case of continuous feed and for the most noticeable attainment of a higher final activity in such a case (Figs. 3 and 4). This additional surface process has been reported and interpreted already (*9*). As previously we assume that the activating and poisoning processes interfere in more than one way. It appears reasonable to assume that the contamination resulting from the hydrocarbon may simultaneously affect the extent of the active surface as well as the H_2–O_2 reaction and the atomic surface mobility induced by it. In particular hydrocarbon species chemisorbed on the surface are expected to lower the mobility of dislodged atoms and therefore the rate of the thermal restructuring of the surface. A stronger efficiency of the activating process should then result. However paradoxical it may appear at first sight, a higher level of activity can therefore be expected from a contaminated surface.

In the present situation the whole consequence of the hydrocarbon addition displays itself in two steps. The poisoning of the available active surface is a fast process and can be quickly observed. The more subtle increase of activation can be evidenced only if the catalyst spends a sufficiently long time under the contaminating conditions. That is the result of a shift in the steady state arising from two opposite effects, namely, the surface disturbance by the H_2–O_2 reaction and the thermal restructuring of the disturbed surface. If the latter process is assumed to be impeded by the presence of carbonaceous species on the surface the opposite activation process is expected to become more efficient. Compared to usual poisoning more time is needed in order to obtain the full extent of such effects as they imply a structural adjustment of the surface.

CONCLUSION

The kinetic situation which prevails under steady conditions appears rather intricate in our case. Numerous surface processes must be invoked in order to account for the whole catalyst behavior. The necessity of doing so appears when *the complete transient behavior* of the catalyst to the various sudden changes imposed to any kinetic factor is taken into consideration.

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