JOURNAL OF CATALYSIS 36, 379–384 (1975)

The Steady State Catalytic Activity of Nickel in Ethylene Hydrogenation as Essentially Due to the Promoting Effect of Oxygen Traces

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Received January 28, 1974

The catalytic activity of nickel in ethylene hydrogenation is shown to result quasi-completely from active sites created by the partial or entire simultaneous conversion into water of the oxygen traces carried by the reacting mixture. The ethylene hydrogenation and the water synthesis appear then to be coupled upon the catalyst surface, the former proceeding on the active centers generated by the latter.

As the rate of disappearance of active centers increases with temperature whereas the total oxygen conversion is limited, a maximum occurs in the steady-state activity versus temperature. This scheme is proved by the disappearance of this optimum, with a considerable lowering of activity, following a drastic purification of the reacting mixture. The maximum and activity both reappear when the purification becomes less rigorous.

INTRODUCTION

We recently reported (*1*) the existence of transient states for nickel catalysts in ethylene hydrogenation following different pretreatments of the metal and we proved (*2*) that they are due to traces of oxygen being present (even at some 1/10 ppm) either in the reacting mixture or in the gases used for the pretreatments. Our interpretation is that the change in the catalyst activity with time is the result of a modification in the nature of its surface. In this particular case, we proposed that the production of water catalyzed by the surface of nickel is accompanied on this surface by a production of active sites for ethylene hydrogenation. It is probable that these sites are produced when oxygen adsorbs onto the metal and that they are released by water desorption. Other significant results were obtained with either nickel (*3*) or other metals (*4,5*) that confirm the hypothesis we propose and for which we could not find any substitute. The particular alternative hypothesis that oxygen was involved in the formation of catalytically active surface species was discussed and discarded because of a number of experimental data we considered in the above-mentioned papers. This conclusion agrees with the present view of several authors who think that chemisorptions may disturb the surface of the adsorbent (notably in the Ni/O_2 system) (*6,7*) and also with the observations of Gwathmey and co-workers who established that mobility was acquired by the copper surface during water synthesis (*8–10*).

Moreover, nickel is well known to show a remarkable feature in ethylene hydrogenation, namely, the occurrence of a maximum in its catalytic activity versus temperature. Concerning this maximum, it is important to notice that even a limited bibliographic research gives indications which are at variance with the usually accepted depopulation hypothesis. Let us only remember that Miyahara and Naruni (*11*) observed a shift in the temperature of the maximum by mere repetition of their determinations in apparently similar conditions with the same catalyst and that Schwab and Goetzeler (*12*) observed a maximum with a rising temperature only.

Taking into account the hypothesis formulated above and the correspondence between the rate changes of ethylene hydrogenation and oxygen consumption as the temperature rises (*2*), we proposed in a recent preliminary note another possible explanation precisely based on the effect of oxygen traces which are inevitably present in the feed mixture. Above a certain temperature, the rate of production of active sites can no longer rise (O_2 being almost completely used up in the feed gases of a flow-type reactor) and indeed they would disappear more and more quickly. In a somewhat similar case, in which, moreover, the Arrhenius law was apparently also not observed, Duval and coworkers (*13–16*) showed that the usual hypothesis of the surface depopulation is not right and developed an interpretation akin to ours.

We now provide new experimental confirmations of our viewpoint of the determining effect of oxygen by examining the results obtained when using the most rigorous purification of the reacting mixture from oxygen that we can devise.

METHODS

The reaction has been carried out with a flow-type apparatus and with chromatographic analysis of the products. The reacting mixture is obtained by adding ethylene (Air Liquide 99.99%) to hydrogen diffused through a palladium thimble. Ethylene is purified from O_2 by a Deoxo cartridge and from water through a coil immersed in dry ice, before entering a flow rate regulator.

In all the experiments here described, the reacting mixture is composed of about 5% ethylene and 95% hydrogen and its flow rate is 133 ml/min, a value imposed by the simultaneous use of an oxygen meter (Engelhard Mark II electrochemical meter); the most sensitive range of the meter is 0–10 ppm, which ensures the measurement of as low a content as 1/10 ppm and gives the possibility to estimate about 10 ppb.

The nickel catalysts are either massive or supported on graphitized carbon black (Spheron 6; Cabot; 110 m^2/g). The massive samples are made of ribbon pieces (Material Research Corporation; 99.99%) or of rod filings (Johnson Matthey; 10 ppm total impurity). The supported sample is prepared by impregnating the support by 1.8 cm^3/g of a nickel nitrate 1.65×10^{-2} *M* solution (Hopkin and Williams, Analar) drying and reducing to the metal.

More details about apparatus and procedure are given below as needed because they have been changed from one experiment to the next in the course of our work.

RESULTS AND DISCUSSION

Steady State Determinations

First we establish the curve (No. 1, Fig. 1) of the stationary activities versus temperature of a nickel ribbon (7 cm long), placed in the axis of a quartz U-tube (4 mm i.d.). The procedure is the following. The ribbon is heated in the reacting mixture from room temperature to 310°C and maintained at this temperature until a stationary rate of ethane production is established. The rate is then measured at different and fixed temperatures proceeding by decreasing steps. For each determination, caution is taken that a period of stationary activity is well obtained; this is attained quickly enough at temperatures higher than about 250°C, whereas 15 to 20 hr are necessary at about 150°C.

The operation is made again by rising

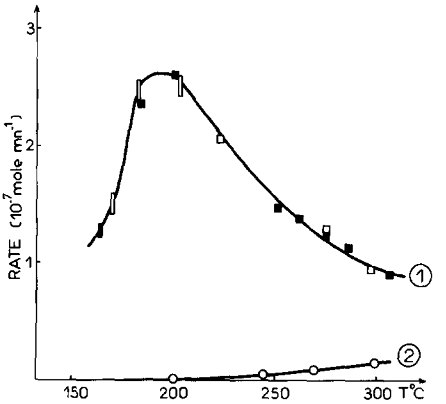

FIG. 1. Stationary activities versus temperature for a Ni ribbon (2.8 cm^2 geometric area). (■) decreasing temperatures, (□) increasing temperatures, 1.3 ppm O_2; (○) oxygen content < 10 ppb.

steps with the same remarks as to the establishment of a steady state. After the experiment the oxygen meter allows us to verify that the content of oxygen in the inlet reacting mixture keeps the same value as before (1.3 ppm).

As to the second set of experiments, our object has been to purify the reacting mixture with regard to the oxygen so that we measure only the intrinsic activity of the metal and not that due to the active sites created by water synthesis. Now, it is not easy to carry out a purification from ultimate traces when each "Swagelock" fitting and especially each valve contribute to make air traces present in the reacting gas. After some unsuccessful experiments, we chose a two-stage reactor, constituted by two welded quartz tubes; each is the same as the one used previously and contains a similar length of ribbon. Each of these two tubes can be independently heated. The first reactor which contains a 6 cm ribbon is heated to 320°C and kept at this temperature during all the experiment. The second reactor contains the same 7 cm ribbon as used previously. At room temperature, its contribution to the reaction cannot be measured, which enables the determination of the precatalyst stationary activity. By subtracting this activity from the total activity measured when the catalyst is heated at a needed temperature, we then obtain the proper activity of this catalyst at this temperature.

We proceed in every point in the same way as previously to draw the rate curve versus temperature (curve 2, Fig. 1). The recorded response of the oxygen meter does not show any deflection as the catalyst temperature varies. This last point ensures that the O_2 content at the entrance of the second reactor does not exceed 10 ppb.

Figure 1 clearly shows that the activity is almost entirely due to the presence of oxygen traces and that when they are eliminated, the very low measured rate does not present any maximum with temperature. Besides, we notice that for curve 2 steady values of the rate are at once obtained except for the first experiment at 300°C, a temperature at which we observe a progressive decrease of the activity. This decrease is explained as the disappearance of the active sites produced when the metal surface, first oxidized, is reduced.

It is possible, however, that the smallness of the surface used for these experiments (2.8 cm^2 geometric area) reduces the intrinsic activity of the metal to an extremely small value and it may be thought that the lack of a maximum on curve 2 in Fig. 1 is not really significant in as much as it would be made invisible because of the necessarily limited sensitivity of the product analysis. For this reason, we thought it desirable to carry out the same experiments but on larger surfaces.

Dynamic Determinations

Measuring stationary activities at different temperatures demands that the oxygen content is constant through the entire experiment (1 wk or more). This is the reason why we prefer the much more rapid procedure which consists in following the activity while a program of temperature is applied. We already said that heating a catalyst which has accumulated oxygen at a low temperature causes a transient excess of active sites with regard to the stationary state and then the occurrence of a maximum irrelevant to any gaseous O_2 consumption. Therefore, though the decrease of temperature is less linear than the rise, we chose a program of decreasing temperature. The curves so obtained keep the same aspect as the curves of stationary activities especially as far as the sign of the rate variation is concerned. The chosen rate of cooling is 6 deg./min for all the here described experiments but it obviously lessens below 150°C.

We first used as a catalyst the same ribbon as in the previous experiments but 20 times more in quantity, the "precatalyst" remaining the same (6 cm long). The curve of activities versus temperature still shows a maximum. To keep our assumptions, we must assign it to an insufficient purification which needs here to be drastic because we are using large surfaces. We were therefore led to choose as a "precatalyst" a supported silver catalyst which is not very active in the hydrogenation of ethylene and which may be used in more important amounts though with a limited activity in ethane production. Curve 1 of Fig. 2 (magnified in the left upper corner) shows the activity variation when the precatalyst is at about 250°C. The very clear improvement of the curve so obtained prompts us to think that the nickel did not ensure a sufficient purification. Moreover, when heating the silver precatalyst at 550°C we see the curve (No. 2, Fig. 2) approximating to that which ought to be expected according to the Arrhenius law while at the same time the activity does decrease. The only change in the slopes which supersedes the maximum cannot obviously be observed if the rates are reported on the same plot as that used when the precatalyst is at the dry ice temperature (curve 3) or, moreover, ethylene is not at all purified from its oxygen (Deoxo-cartridge by-passed) (curve 4). The chronological order in which these four different curves have been obtained with the same catalyst is important because it proves that the disappearance or dwindling of the maximum is not due to an irreversible change of the catalyst.

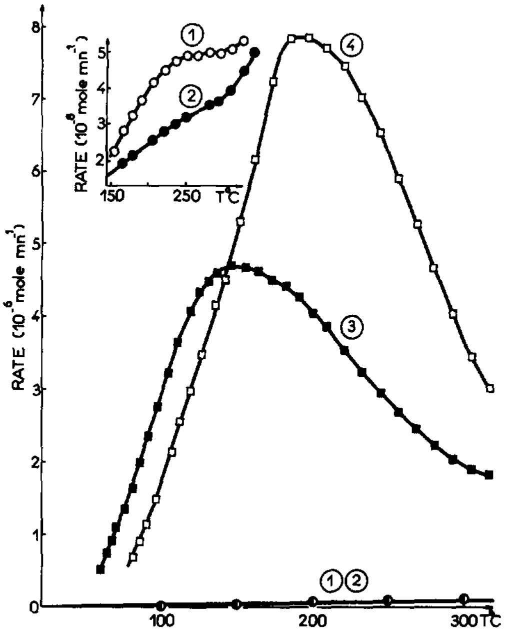

FIG. 2. Activities versus temperature for Ni ribbon (56 cm^2 geometric area). Program of decreasing temperature 6 deg./min. Different O_2 contents. Left upper curves = 20 times magnified.

Figure 3 shows the same type of procedure with a progressive disappearance of the maximum. These results relate to 80 mg of nickel filings (80–100 μm). The curves are obtained in the following order:

1. Silver precatalyst at about 280°C;
2. Silver precatalyst at 550°C;
3. Silver precatalyst at dry ice temperature.

Figure 4 shows the pattern obtained by use of a supported nickel catalyst (55 mg graphitized carbon black). The purification is performed through two stages, first by silver wool (about 3 g) and then by a nickel precatalyst identical to the proper catalyst

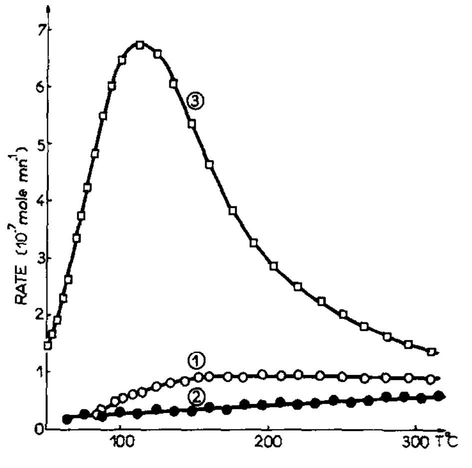

FIG. 3. Activities versus temperature for 80 mg Ni filings (80–100 μ). Program of decreasing temperature 6 deg./min. Different O_2 contents.

(50 mg). The decrease or increase in activities is here displayed as a consequence of the purification efficiency again. The curves are drawn in the following way:

1. Silver is heated at 450°C and nickel precatalyst at 250°C;
2. Silver is kept in dry ice and nickel precatalyst at room temperature;
3. The two precatalysts are at dry ice temperature;
4. The two precatalysts are at room temperature and the preliminary purification of ethylene is suppressed.

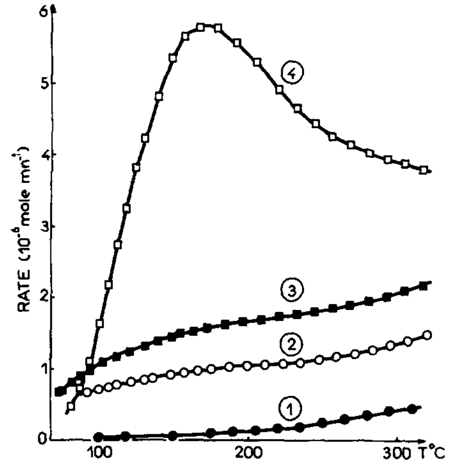

FIG. 4. Activities versus temperature for the supported catalyst. Program of decreasing temperature 6 deg./min. Different O_2 contents.

Remarks About the Dynamic Determinations

We should point out that, for all the curves described here, we took care to verify that the precatalyst activities did not significantly change between the beginning and the end.

We must add that plunging one of the precatalysts into dry ice cannot explain any restoring of activity owing to the removal, for instance, of a condensable impurity because throughout these experiments we always took care to place such a trap just before the catalyst.

Figures 2 and 4 need a comment: they allow us to observe that, at the lowest temperatures, the activities relative to certain contents of oxygen exceed those relative to other higher contents, which seems at variance with our previous assertions. To explain completely that phenomenon, we must compare it with other observations too long to be developed here and so we discuss it elsewhere (*3*). In order to sum up we can say that it is the manifestation of an inhibition due to the occupation of a part of the active sites by oxygen and that it appears at sufficiently low temperatures.

CONCLUSION

The results reported here clearly show the essential influence exerted by oxygen upon ethylene hydrogenation. The comparison of the activities of different nickel samples, when traces of this element are present or not, shows that by far the largest part of the chemical transformation takes place on the active sites produced by the synthesis of water which occurs at the same time. This is so even when the production of water may remain unsuspected because of the vanishingly small quantities of oxygen set in action, but it is obvious that the phenomenon plays a more important part the higher is the oxygen content.

For instance, the stationary rate measured at 220°C on 2.8 cm^2 of nickel ribbon is multiplied by 6 when the oxygen content changes from 1.3 to 8 ppm.

The promoting influence of oxygen on this same hydrogenation catalyzed by platinum has already been observed (*17,18*) and, furthermore, in another case (*19*). Nevertheless our interpretation put forward here about nickel, but which may be extended to platinum and other metals of great catalytic interest [as we shall show in following papers (*4,5*)], is completely different from that proposed by Schlatter and Boudart (*17*). The main experimental argument which leads us to refute their viewpoint is that metal "deactivation" is observed even in the absence of hydrocarbon and therefore is a property of the system Metal/O_2/H_2 (*1*).

Whatever its interest may be, we do not think that the most important conclusion from this work consists in the disappearance of a maxinum of activity with regard to temperature. No one, after all, has ever brought convincing proofs to make the depopulation of the surface responsible for the occurrence of an optimal activity versus temperature. More interesting seems to be the production of active centers on the metal surface *by a chemical way* and that this production may be coupled with another chemical transformation. This situation compares with the earlier use of the ortho- para hydrogen conversion to demonstrate the formation of free radicals in hydrocarbon pyrolysis.

Another type of analogy has already been formulated in general terms by Boudart (*20*) comparing any heterogeneous catalytic reaction to a homogeneous chain reaction. What is new, however, consists in the possibility offered by the present case to extend the analogy completely, saying that the initiation process of a homogeneous chain reaction is here replaced by the active site production due to water synthesis whereas the termination step finds its equivalent in the relaxation of the activated surface.

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