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NOTES

Unexpected and Progressive Self-Reactivation of Rhodium Catalyzing the H_2–O_2 Reaction after an Immediate Inhibition by C_2H_4 Added to the Reactant Mixture: Parallel Activation in C_2H_4 Hydrogenation

We have already reported (*1–6*) that the best way of explaining the promoting influence of O_2 on the catalytic activity of various transition metals (and especially Rh) in the hydrogenation of C_2H_4 appears to be the structural sensitivity of the metal surface to the H_2–O_2 reaction. The latter is able to induce the mobility of the metal atoms and so to generate particular configurations which are considered as possible active catalytic centers. The spontaneous thermal restructuring of the surface gives these centers a limited lifetime and this point is most important in explaining the memory effects of the catalyst due to various pretreatments or procedures. When the reaction is carried out for long enough times, the atomic mobility which it induces results in gross surface rearrangements that eventually become visible by electron or optical microscopy (*5, 6*). These observations lend strong support to our model.

Nevertheless, the activating influence of O_2 used as a pretreatment agent has been known for a long time (*7–16*), even though O_2 has never been wittingly used as a permanent trace in the reactant mixture up to now. This activating influence was first explained as resulting from the burning off of carbonaceous residues which accumulate on the surface in the course of the reaction (*10, 11*). A different view (*12–16*) then emerged on the basis of the possible positive influence of the oxygen which could remain on or near the surface even under the reducing conditions of the reaction.

Our present interpretation does not deny either of these two assumptions. However, we have previously reported (*1, 2, 6*) several experiments which clearly show that the major part of the O_2 effect must in fact be ascribed to the action that O_2 *and* H_2 can exert on the surface either *simultaneously* or *successively*. Thus the so-called "O_2 effect" cannot be accounted for as the mere result of O_2 only, as is suggested by a cleaning or a chemically induced effect.

Whatever the effect may be, we have tried to reach a deeper insight into the kinetic role of carbonaceous residues by looking for it in the H_2–O_2 reaction. To do so, we have added C_2H_4 suddenly to the H_2–O_2 reactant mixture after the steady state of activity has been reached in H_2 oxidation. The subsequent phenomena constitute an indirect and novel illustration of the effect under study.

The kinetic determinations have been carried out at atmospheric pressure in a dynamic reactor, using experimental arrangements and procedures previously described (*1–3, 6*). The temperature range is the same (100–300°C) and the H_2–O_2 reactant mixture is mainly constituted of ultrapure H_2 carrying 10 to 30 ppm O_2 in order that the present results relate to the same conditions as those used previously. When C_2H_4 is added to the reactant mixture, its content is 5% whereas the O_2 content is maintained. The analysis of the outlet gas with a conventional FID chromatograph (Intersmat, IGC 12 F) and an electrolytic O_2 meter (Engelhard, Mark II) makes it possible to know the rate of C_2H_6 production and the amount of O_2 reacted.

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The experiments consist mainly in suddenly submitting the catalyst to the action of C_2H_4 once its steady state of activity has been reached in the H_2–O_2 reaction. Conversely, when the steady state is established with respect to both reactions (C_2H_4 + H_2 and H_2 + O_2) C_2H_4 is suddenly removed. To effect instantaneous transitions, the ternary mixture (H_2, C_2H_4, O_2) is substituted for (H_2, O_2) (or conversely) by the rotation of a four-port switching valve rather than by merely adding (or removing) C_2H_4.

An *immediate* decrease of the activity in the H_2 oxidation is expected from the C_2H_4 introduction, due to the fast occupation of the surface by the hydrocarbon. Moreover, if the usual deactivation which follows an activating O_2 treatment in C_2H_4 hydrogenation (*1*, *2*, *6*) is supposed to be due to the progressive formation of carbonaceous residues, an additional deactivation in the H_2–O_2 synthesis should *progressively* occur. That deactivation should occur during a similar time and display a similar relative amplitude as can be observed in the hydrogenation of C_2H_4 after an activating O_2 treatment has been applied [see (*6*, Fig. 4)]. In the same manner, the rate of C_2H_4 hydrogenation should decrease from the value measured initially (which refers to a surface free from carbonaceous residues) down to the value corresponding to the contamination level imposed by the operating conditions.

In fact, the catalytic response is strikingly different and depends on the temperature of the experiment, as described below:

(1) If the temperature is high enough (higher than about 250°C) the steady state of activity is immediately reached for both reactions. No variation is observed in the H_2–O_2 reaction inasmuch as nearly all of the O_2 is reacted and no deactivation proceeds later in the H_2–O_2 reaction or in C_2H_4 hydrogenation.

(2) A still more surprising and meaningful response is displayed between about 100 and 200°C. As illustrated in Fig. 1, the introduction of C_2H_4 into the reactant mixture (Fig. 1, A) causes an immediate decrease of the rate of the H_2–O_2 reaction. Soon afterwards the rate increases and about 10 h later levels off to nearly its initial value. The rate of C_2H_4 hydrogenation increases simultaneously and reaches its steady value after an equal time.

When C_2H_4 is removed by replacing the (H_2, C_2H_4, O_2) mixture by the previous (H_2, O_2) mixture (same O_2 content), the catalyst response (Fig. 1, B) is equally meaningful. The inhibition of water synthesis due to the partial occupation of sites by C_2H_4 ceases immediately and brings about an acceleration of the H_2–O_2 reaction. However, the rate of that reaction soon passes through a maximum and progressively decreases until the initial steady state is eventually reached. The same slow deactivation of the catalyst should be involved in the hydrogenation of C_2H_4 as well but cannot be continuously observed since it is caused precisely by the removing of C_2H_4. In order to make it visible, at the end of the deactivation C_2H_4 may be reintroduced. This makes the deactivation visible and, if the hydrocarbon is maintained, causes the exact repetition of the events previously described.

The first conclusion we can deduce from Fig. 1, A and Fig. 1, B is that the *steady* rate of the H_2–O_2 reaction remains the same if C_2H_4 is present or not.

In a separate experiment, the sample was flushed with a mixture (95% He, 5% C_2H_4, 30 ppm O_2) in order to detect any reaction between O_2 and C_2H_4. The O_2 consumption due to that reaction is unobservable throughout the whole range of temperatures.

The above results are interpreted as follows. First, the experiments clearly show that the building up of carbonaceous residues is a poor way of explaining the whole behavior of the catalyst when it is exposed to C_2H_4. The existence of such poisoning residues is not questioned, as we shall later give new information about their kinetic

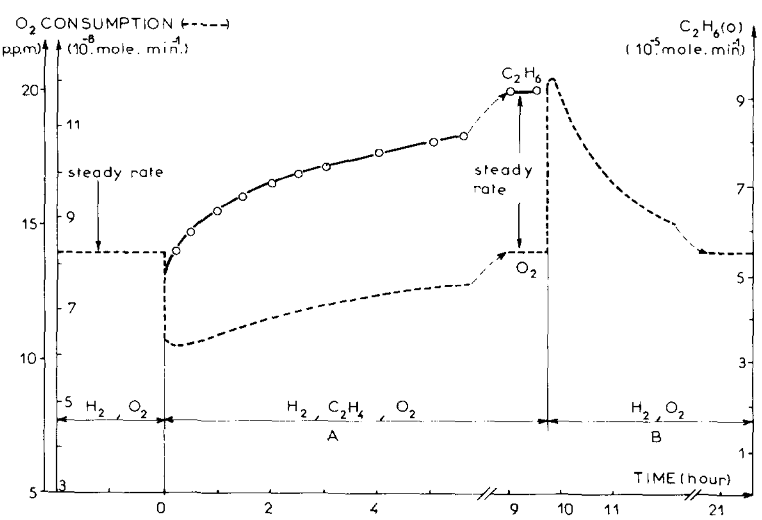

FIG. 1. Variation of the rate of the H_2–O_2 reaction as a function of time after adding (A) or removing (B) C_2H_4. The steady state had been reached before addition or removal. Parallel variation of the rate of C_2H_4 hydrogenation (part A of the figure). Temperature: 125°C. Reactant mixtures H_2 + 30.5 ppm O_2 (before part A; part B) 95% H_2 + 5% C_2H_4 + 30.5 ppm O_2 (part A).

behavior. But the deactivation expected from their formation is not here the prevailing process since the catalyst *reactivates* instead at a medium temperature in such a manner that its activity in H_2O synthesis remains higher for several hours once the hydrocarbon is removed. Some radically new assumption must obviously be put forward in order to explain such a bewildering behavior.

Now, if we examine the two types of response of the catalyst to the introduction of hydrocarbon in the (H_2, O_2) mixture, the simplest situation is unexpectedly displayed at the highest temperatures, where there appears to be no mutual hindrance of the two reactions. They must therefore occur with small coverages of active sites. We have previously explained (*1*, *2*, *6*) that these sites are generated by the occurrence of the H_2–O_2 reaction, which induces the surface mobility. If ethylene coverage of the active surface is small, the H_2–O_2 reaction is almost unaffected by the hydrocarbon and the number of active centers remains practically constant when introducing C_2H_4. This is the reason why the steady state of activity is immediately reached, contrasting with the more usual transient behavior of the catalyst (*1*, *2*, *6*). Once more the transient behavior in C_2H_4 hydrogenation appears as the result of that of the H_2–O_2 reaction.

The situation is quite different at lower temperatures, for which C_2H_4 coverage is no longer negligible and causes the initial quick decrease of the H_2–O_2 reaction rate. No decreasing rate happens for C_2H_4 hydrogenation. On the contrary, it speeds up immediately but slowly as the H_2–O_2 reaction does after a short time. That the rates simultaneously increase for both reactions, in spite of the inhibition exerted by C_2H_4 upon the O_2 reaction, clearly means that new active sites are being created on the surface. It might be imagined that a new active surface, differing from the initial one in chemical compositioin or structure, is progressively being formed due to the exposure to C_2H_4. However, it would be most unlikely that the final activity level for the H_2–O_2 reaction would be nearly the same as the initial activity. Furthermore this assumption would be at variance with the deactivating effect usually ascribed to the hydrocarbon.

A simple explanation can be found that demonstrates that *the inhibition itself* could cause a further *overall activation* of the catalyst. In agreement with our views let us assume that when the H_2–O_2 steady state has been established, the reaction occurs mostly on the active sites that have been generated during the transient period which precedes the establishment of the steady state. These active sites, S*, are less numerous but more active than the normal sites, S. They disappear spontaneously due to the thermal restructuring of the surface and the constancy of their number results from the fact that the rate of their disappearance, r_d, is equal to that of their production, r_p. The latter is ensured by the small contribution to the overall rate of the H_2–O_2 reaction, which must be assigned to the less active sites, S, of the surface. Because of their lower activity, the O_2 coverage is higher on sites S than on S* and this is all the more expected as the temperature is lower. It follows that when C_2H_4 is introduced into the reactant mixture, sites S* are more affected by it than S and we may assume that the rate of water synthesis on S remains nearly unchanged whereas the rate on sites S* is greatly diminished due to their partial coverage by C_2H_4. On the other hand, the coverage of some S* by C_2H_4 results in the catalyst activity for C_2H_4 hydrogenation.

We may now reasonably conceive that the dislodged atoms of which the S* sites are made lose much of their mobility, and hence their ability to disappear, when a chemical species is adsorbed onto them. We may then expect that, in addition to inhibiting the H_2–O_2 reaction, the adsorption of C_2H_4 also inhibits the spontaneous restructuring of the surface and so causes a decrease of r_d while r_p is maintained nearly equal to its initial value r_p^0. An activation period must then result since

$$r_d < r_p = r_p^0$$

until the equality

$$r_d = r_p \ (= r_p^0)$$

is restored. But when that is the case the number of sites free from C_2H_4 and so able to disappear is just the same as initially. The same situation as initially is then restored for the H_2–O_2 reaction, which therefore occurs at the same rate. Obviously some of the newly created S* sites are occupied by C_2H_4 as they are formed and that causes the activation of C_2H_4 hydrogenation to parallel that of the H_2–O_2 reaction since both reactions occur on a growing number of active sites. The ratio of S* sites that are covered by C_2H_4 must keep constant. Its value can be estimated from the relative lowering of the rate of the H_2–O_2 reaction when C_2H_4 was introduced and from the relative increase of the same rate when C_2H_4 was removed inasmuch as the H_2–O_2 reaction is considered to occur mainly on the S* sites. The two ratios in question can easily be estimated from parts A and B of Fig. 1 by extrapolating the rising curve of part A (relating to the H_2–O_2 reaction) or the decreasing curve of part B until the times of C_2H_4 introduction or removing. The values obtained (respectively 0.71 and 0.67) are in good agreement.

When higher temperatures are reached (in the neighborhood of 180–200°C), S sites can contribute more to the H_2–O_2 reaction and their oxygen coverage is therefore expected to decrease. Their inhibition by C_2H_4 becomes possible so that it might happen that the same activity level of the catalyst for the H_2–O_2 reaction would not be exactly restored at the end of the transient period following C_2H_4 introduction. However, this observation is rendered difficult because the high percentage of the O_2 reacted at such temperatures makes the difference necessarily very small.

These experiments are complementary to those previously reported (*1*, *2*, *6*), especially in the case of Rh (*6*). We had formerly shown the high promoting influence of O_2 contained in the reactant mixture (C_2H_4 + H_2) and we have now examined the effect of C_2H_4 added to H_2 + O_2. In either case the situation is simpler at high enough temperatures. In the present case, as C_2H_4 is added once the steady state of the H_2–O_2 reaction has been reached, the rate of the H_2–O_2 reaction remains constant and the steady state of C_2H_4 hydrogenation sets up immediately. At lower temperatures, the expected inhibition of the H_2–O_2 reaction by a partial coverage of active sites by C_2H_4 can be transiently observed but does not constitute the most meaningful feature of the catalyst behavior since there is a spontaneous and progressive disappearance of this inhibition whereas a parallel activation affects C_2H_4 hydrogenation. The reverse behavior is observed after C_2H_4 has been removed and the catalyst activity in the H_2–O_2 reaction remains better for several hours.

Mutual hindrance (and not acceleration) is expected from the simultaneous occurrence of two reactions on the same surface unless one of the partners reacts with the catalyst and causes it to change into a more active compound. Not only is nothing like that to be expected between Rh and C_2H_4 but hydrocarbons are usually considered responsible for the formation of a carbonaceous layer which deactivates catalysts. It seems therefore that no possibility can be found to explain such an unexpected behavior from usual views.

New perspectives arise if one accepts the possibility that a reaction causes the creation of active sites on a solid surface. The total number of active sites present on the surface at any time derives then from simultaneous production and disappearance processes in much the same manner as free radicals appear and disappear in chain reactions through initiation and termination steps. We can easily imagine that either of these processes may be speeded up or inhibited by one or another of the reaction partners as well as any of the usual elementary steps of reactions. Such assumptions allow one to understand a catalyst behavior which would otherwise remain paradoxical. Analogous behavior is expected for any other moderate inhibitor (e.g., other light hydrocarbons) added to the H_2–O_2 mixture. If a reaction other than the H_2 oxidation led to the observation of such phenomena its autocatalytic property might be invoked.

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