

Long-Induction Period in the Oxidation of Ethylene over a Silver Catalyst

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An extraordinarily long-induction period has been observed in the oxidation of ethylene over a silver catalyst used in the oxidation of acetaldehyde at 130–180°C. It is found that the induction period is caused by the existence of stable adsorbed intermediates which are formed in aldehyde oxidation. The nature and the reactivity of the intermediates show the same behavior as the reaction intermediates in the oxidation of ethylene, suggesting common intermediates in both reactions. The intermediates react with H₂ to form acetic acid and ethyl alcohol, and are decomposed into CO₂ and H₂O by the reaction with oxygen. The surface coverage of all the intermediates is estimated to be from 0.73 to 1.46 depending on the gas composition and the reaction time in acetaldehyde oxidation, suggesting their multilayer adsorption. It has been confirmed that the intermediates have a similar nature and reactivity to solid silver acetate, indicating a silver acetate form as one species of the intermediates. © 1984 Academic Press, Inc.

1. INTRODUCTION

As has been demonstrated in our previous papers (1–4), when ethylene oxidation is carried out on silver at temperatures lower than 110°C, a stable intermediate is formed on the surface in appreciable amounts. This intermediate has a characteristic nature and reactivity: it reacts with oxygen to form equal amounts of carbon dioxide and water, and it reacts with hydrogen to form acetic acid. The surface coverage of the intermediate strongly influences the mode of the transient behavior of ethylene oxidation. The detailed analysis of both the transient behavior of the intermediate and the reaction leads us to the conclusion that the intermediate is one of the species in the passway of the complete oxidation of ethylene.

Our subsequent interest is focused on the detailed structure of the intermediate: how many species constitute the intermediate or what their reactivities are. To elucidate these questions, it is necessary to prepare appreciable amounts of them on the surface. Our speculation concerns acetalde-

hyde, which has been considered as one of the intermediates in ethylene oxidation (5). According to our experimental results, ethylene reacts with surface oxygen to form acetaldehyde and is immediately converted into the intermediates in the complete oxidation, a certain amount of which are accumulated on the surface at the reaction steady state, suggesting that the decomposition of the intermediates should be one of slow steps (3, 4). One may thus expect that the oxidation of acetaldehyde will form the intermediates on the surface more than ethylene oxidation does.

In the present study, the oxidation of acetaldehyde is used for the detailed analysis of the intermediates relating to the oxidation of ethylene. The transient response method (6–8) is also applied to follow the dynamic behavior of the intermediates during the reaction.

2. EXPERIMENTAL METHOD

A silver catalyst was prepared by reducing silver oxide with hydrogen. Silver oxide in which a small amount of potassium sulfate had been well mixed was coated on α -

Al_2O_3 of 20–42 mesh, and the sample was sieved so as to become 12–14 mesh. The sample packed in a Pyrex glass reactor was carefully and slowly reduced by a pure-hydrogen stream at 50°C for 12 hr and then at 100°C for 12 hr. The composition of the catalyst prepared thus was 67.6 g Ag, 0.367 g $\text{K}_2\text{SO}_4/194.6$ g $\alpha\text{-Al}_2\text{O}_3$, and the BET surface area was 0.3 m^2/g Ag.

The total gas flow rate used was 160 (± 2)NTP ml/min through all experiments and the gas composition was changed by using N_2 or He as a diluent. Intraparticle and external mass transfer effects were confirmed to be negligible by testing the behavior of the reaction rates depending on the catalyst particle sizes and the gas flow rates, respectively, at 123 and 160°C . Three flow-controlling systems were prepared for the transient response method, all of which could prepare the different gas compositions with the same flow rate. The stimulus of the gas composition change was put into the reactor by using two four-way valves which were attached between the three systems. The response of the gases in the outlet of the reactor was followed by three gas chromatographs in order to follow the responses of all the components as continuously as possible.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Induction Period in the Oxidation of Ethylene

Interpretation of the long-induction period. The oxidation of ethylene and acetaldehyde is initiated at temperatures higher than 80 and 130°C , respectively, producing ethylene oxide, carbon dioxide, and water for the former, and CO_2 and H_2O for the latter. Acetaldehyde oxidation has a long decay of catalytic activity over a period of more than 24 hr, reaching a quasi-steady state level less than one-tenth the initial reaction rate.

Figure 1 showed an example of the transient responses repeated between the two

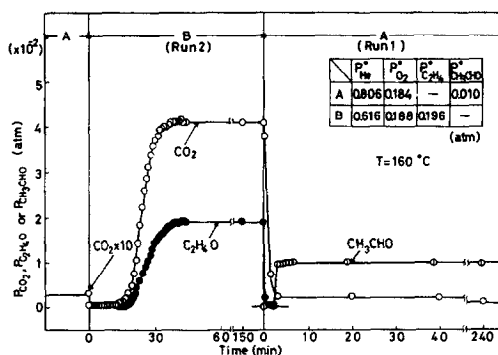


FIG. 1. Transient responses between acetaldehyde and ethylene oxidation.

reactions: the reaction gases were changed into either $\text{CH}_3\text{CHO}-\text{O}_2\text{-He}$ stream (Run 1) or the $\text{C}_2\text{H}_4-\text{O}_2\text{-He}$ (Run 2) at 160°C . Noting the steady state rates in the two reactions, one may recognize reproducible activity indicating that running one reaction on the catalyst caused no harmful effects on the latter reaction. In contrast, at the transient state in the oxidation of C_2H_4 , Run 2 clearly showed an extraordinarily long-induction period of more than 15 min. Interestingly, the length of this induction period can be related to the absolute value of the

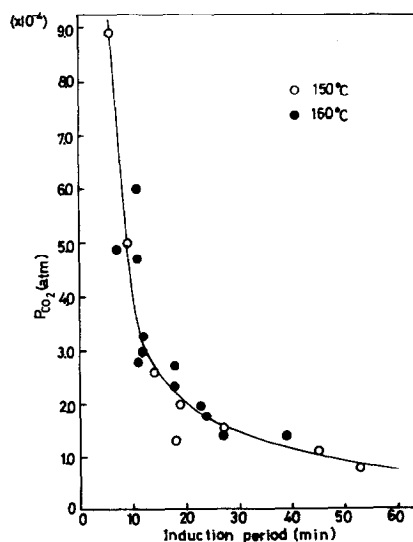


FIG. 2. Relation between P_{CO_2} in Run 1 of Fig. 1 and the induction period in Run 2 of Fig. 1.

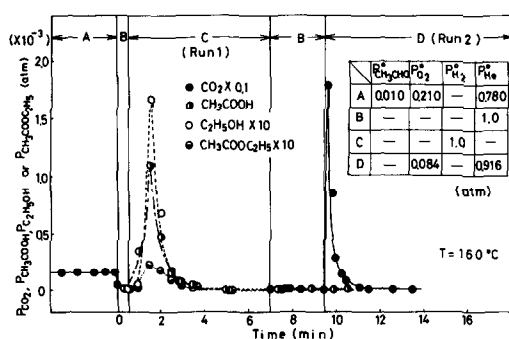


FIG. 3. Confirmation of the intermediates formed in acetaldehyde oxidation.

CO₂ formed at the quasi-steady state in Run 1. Namely, the lower the CO₂ value at the quasi-steady state in Run 1 the longer the induction period in Run 2, more than 50 min in some instances, as shown in Fig. 2.

Our interest is focused on the reason for the appearance of the induction period, and on what is happening on the surface during the induction period. One possible explanation that can reasonably be considered is the blocking effect of the adsorbed intermediates which are formed in acetaldehyde oxidation. Figure 3 clearly proves the validity of this idea. The surface used for the oxidation of CH₃CHO was flushed by He for 5 min and then a pure-H₂ stream was introduced into the reactor (Run 1). Run 1 definitely demonstrates the formation of three components: a large amount of acetic acid (1.0×10^{-7} mol/g Ag) and small amounts of ethyl alcohol (1.2×10^{-8} mol/g Ag) and ethyl acetate (4×10^{-9} mol/g Ag). This indicates that H₂ reacts with the adsorbed intermediates which are retained on the surface during the He flush. When the O₂-He stream was introduced into the reactor (Run 2), CO₂ and H₂O were formed (H₂O was not shown in the figure).

From the above results, one may conclude that, there are some intermediates (In) which are formed on the surface in the oxidation of CH₃CHO, and the intermediates react with H₂ to produce acetic acid and react with O₂ to produce CO₂ and H₂O.

Similarity of the intermediates between ethylene and acetaldehyde oxidations. Acetaldehyde oxidation proceeds at temperatures higher than 130°C, whereas ethylene oxidation is initiated above 80°C. A comparison of the nature and reactivity of the intermediates between the two reactions should be performed at the same temperature. Figures 4 and 5 visualize the comparison of the reactivity at 91°C between the intermediates formed in the two reactions. In Fig. 4, for acetaldehyde oxidation, three successive Runs (1-3) were carried out and followed by an He flush between the runs. The intermediates were formed in Run 1 at 148°C, and then the temperature of the reactor was decreased to 91°C in He. In Run 2, when H₂ was introduced into the reactor at 91°C, CH₃COOH was clearly formed and its formation was immediately stopped by the subsequent He flush. In Run 3, when the O₂-He mixture was introduced, CO₂ and H₂O were formed with no other products (only CO₂ is presented in the figure).

Runs 1-4 in Fig. 5 were conducted in the same manner as Runs 1-3 in Fig. 4. The transient responses of ethylene oxidation were examined at 91°C on the surface which had been used for acetaldehyde oxidation at 148°C. The induction period of about 40 min appeared similar to that in Fig. 1 at 160°C and the reaction reached a steady state at about 5 hr. After Run 2 had

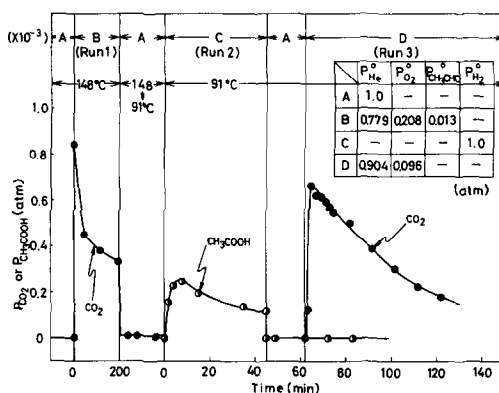


FIG. 4. Reactivity of the intermediates formed in acetaldehyde oxidation at 148°C.

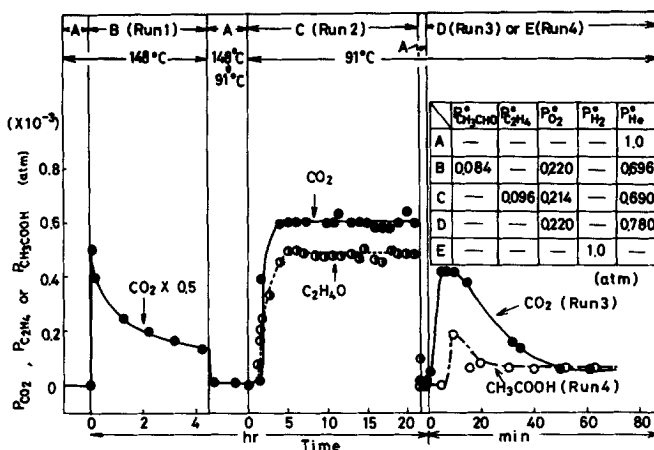


FIG. 5. Reactivity of the intermediates formed in ethylene oxidation at 91°C.

been followed for 22 hr and subsequently by a He flush for 2 min, the $\text{C}_2\text{H}_4\text{-O}_2\text{-He}$ mixture was replaced by either the H_2 stream (Run 4) or the $\text{O}_2\text{-He}$ mixture (Run 3). CH_3COOH was produced in Run 4, and CO_2 and H_2O were formed in Run 3 (only CO_2 is shown in the figure), similar to the responses in Fig. 4.

The above results strongly suggest that some of the intermediates in the two reactions are the same, although the population of the intermediate species is different as will be described in a later section.

3.2. Transient Behavior of the Intermediates and Ethylene Oxidation

Confirmation of the intermediates during the induction period. Our speculation to explain the induction period of ethylene oxidation is focused on the amount of the intermediates which block the adsorption of oxygen. The transient behavior of the intermediates should be a key to understanding the long-induction period. The amount of the intermediates at any period of the elapsed time can easily be evaluated as the amounts of the species formed in the H_2 or O_2 stream.

Figure 6 provides the estimation of their amounts. When the oxidation of CH_3CHO had reached a quasi-steady state, three transient runs were successively performed

as seen in Runs 1–3 of Fig. 6. In Run 1, the long continuation of CO_2 formation in small amounts, in contrast to the absence of $\text{C}_2\text{H}_4\text{O}$, is caused by the slow reaction of the intermediates with surface oxygen, according to the slow rearrangement of the intermediates which will be discussed in detail later. Before initiating the $\text{C}_2\text{H}_4\text{O}$ formation, the mixture was changed into a pure-He stream (Run 2). The formation of CO_2 stopped within 2 min and no other components were formed for 10 min. When a pure-hydrogen stream was introduced into the reactor (Run 3), three components (CH_3COOH , a small amount of $\text{C}_2\text{H}_5\text{OH}$, and a trace amount of $\text{CH}_3\text{COOC}_2\text{H}_5$) were formed, similar to the results in Fig. 3. These successive experiments clearly

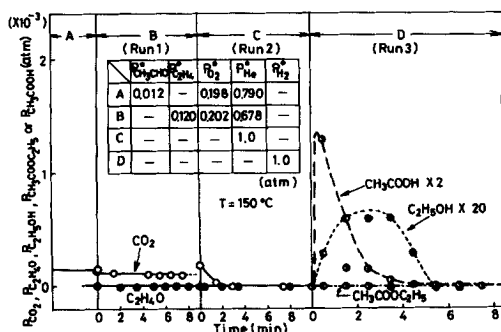


FIG. 6. Confirmation of the existence of the intermediates retained during the induction period.

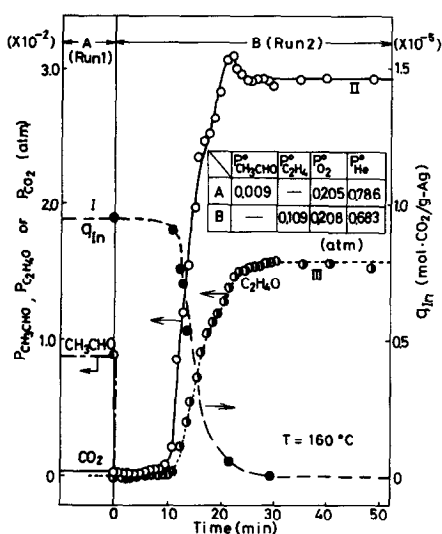


Fig. 7. Transient behavior of the intermediates and ethylene oxidation.

prove the existence of the intermediates retained during the induction period, and the amount of each of the intermediates can be evaluated from the graphical integration of the response curves in Run 3, for example, 9.8×10^{-8} mol CH_3COOH/g Ag and 1.1×10^{-8} mol C_2H_5OH/g Ag.

Comparing between the mode of the response curves in Run 1 in Fig. 3 and Run 3 in Fig. 6, one may recognize their difference: in particular, alcohol in Run 3 of Fig. 6 shows a gradual increase mode in contrast to that of Run 1 of Fig. 3 which has a steep increase mode. There is not enough evidence to explain this difference. One possible explanation is the surface rearrangement of adsorbed intermediates. This rearrangement creates a surface space free from the adsorbed species and changes the reactivity of the intermediates. The surface space is available as active sites for the adsorption of H_2 . In Run 1 of Fig. 3, there is not enough time for the rearrangement compared to Run 3 in Fig. 6.

The variation of the amount of the intermediates can thus easily be evaluated at any period of the elapsed time in the course of the transient state up to reaching the steady state level passing through the in-

duction period. Here, it has been confirmed that the graphical integration of the response curves of the CH_3COOH plus C_2H_5OH formed in the H_2 stream is in agreement with that of the CO_2 formed in the O_2 stream, using a simple stoichiometry for carbon.

Transient behavior of the intermediates. Curve I in Fig. 7 illustrates the transient response of the amount of the intermediates which is estimated for convenience as CO_2 formed in O_2 at any period of the transient time: since the intermediates are decomposed into CO_2 and H_2O when they are exposed to oxygen gas, one can evaluate the total amount of the intermediates at any period of the transient time up to initiating the formation of C_2H_4O , by repeating between two procedures the formation of the intermediates in the CH_3CHO-O_2-He stream and their decomposition in the O_2-N_2 stream. Comparing Curve I to Curves II and III in ethylene oxidation, the period of the initiation of ethylene oxidation exactly agrees with the period of the steep consumption of the intermediates.

As can be seen in Fig. 7, the ethylene oxidation reaches a steady state at a period of 30 min when the amount of the intermediates is greatly reduced to a very small value. From this reduction, one may recognize that the rate of the intermediates decomposition at $160^\circ C$ is faster than that of their formation. Therefore, in industrial conditions higher than $200^\circ C$, the amount of intermediates will be very small, suggesting a different kinetic structure.

Noting Curve I in Run 1 of Fig. 7, the amount of intermediates existing on the surface of the steady state of acetaldehyde oxidation is estimated to be $q_{In} = 9.5 (\pm 1.0) \times 10^{-6}$ mol CO_2/g Ag. This is about four times the amount (2.5×10^{-6} mol/g Ag) of intermediates formed in the oxidation of ethylene at $91^\circ C$ (3). The total number of surface silver atoms has been estimated to be 1.3×10^{19} atoms per m^2 by Scholten *et al.* (9). Assuming that one CO_2 molecule formed from the intermediates resulted

from one surface silver atom, q_{in} corresponds to 1.9×10^{19} sites/m² which is larger than the total number of surface silver atoms. Here, it is confirmed by separate experiments that the intermediates are not formed on the support α -Al₂O₃. This will bring a presumption that for the multilayer adsorption of the intermediates, the surface coverage is from 0.73 to 1.46 depending on the gas composition and the reaction time in acetaldehyde oxidation.

Species constituting the intermediates. Although it is not easy to determine how many species of intermediates there are by using the transient data presented so far, one may presume the presence of at least two different species due to the following reasons: of the two different products, acetic acid and ethyl alcohol exhibited in Figs. 3 and 6, the former is the more oxidized form and the latter is the more reduced form compared to adsorbed aldehyde. It is, therefore, difficult to postulate a common species as a precursor for the two different products of the reaction with H₂. In addition, as will be described in a later section, the silver acetate which is considered as one of the intermediates does not produce ethanol by the reaction with H₂. The intermediates thus consist of at least two different species; one is a precursor to produce CH₃COOH and the other C₂H₅OH.

Here, in aldehyde oxidation, the presence of the weakly adsorbed acetaldehyde is clearly ascertained by following its desorption response curves with the analysis of the diffuse reflectance infrared Fourier transform (DRIFT) spectra, the details of which will be reported later. This weakly adsorbed acetaldehyde leads us to the speculation that aldehyde forms a multilayer on the surfaces. This may be the most probable explanation for the amount of the intermediates estimated from, the formed being CO₂ more than the total silver sites.

3.3. Disappearance of the Induction Period

Four successive Runs 1–4 were per-

formed, each followed by a He flush. In Run 1, the intermediates were formed on the surface in acetaldehyde oxidation. In Run 2, part of the intermediates formed was removed by exposing the surface to H₂ for 1 min, when CH₃COOH was clearly formed. In Run 3, a C₂H₄ (10%)–O₂–He mixture was introduced into the reactor and the responses of CO₂ and C₂H₄O were followed. The two components responded to a steady state within 7 min, indicating the disappearance of the induction period. In Run 4, the steady state level of ethylene oxidation was quickly reproduced.

From the above results, one may recognize that the removal of a small amount of the adsorbed intermediates by reaction with H₂ allows the quick initiation of the oxidation of ethylene. Namely, since the surface used for acetaldehyde oxidation is fully covered with the intermediates, little of the surface is available for the adsorption of oxygen. The removal of the intermediates can create a space for the adsorption of oxygen to initiate the oxidation of ethylene. This is the reason for the disappearance of the induction period. In Run 4, since the surface is almost free from the intermediates, CO₂ and C₂H₄O quickly respond to new steady states.

Here, one may question why CO₂ and C₂H₄O do not show a gradual increase in Run 2 in Fig. 7. In reply to this question, our speculation is that the intermediates need more than two neighboring adsorbed molecular oxygen species for their own combustion. The induction period is used to form such surface space for the adsorption of the neighboring oxygen. During the induction period, the desorption of the adsorbed aldehyde and carbon dioxide and the rearrangement of the intermediates slowly proceed to make the space. Comparing Curves II and III in Fig. 7, one can recognize the initiation period of CO₂ formation as shorter than that of C₂H₄O. This means that the intermediates first decompose and then adsorb molecular oxygen which is active for the formation of C₂H₄O

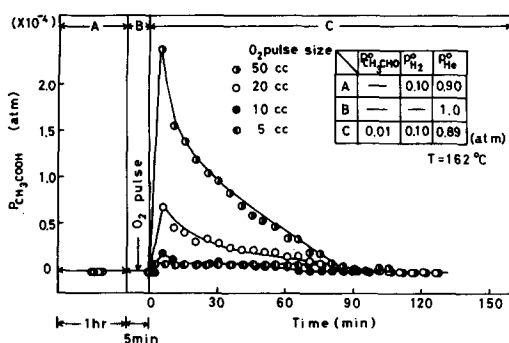


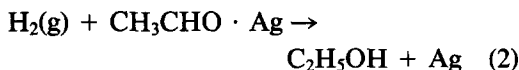
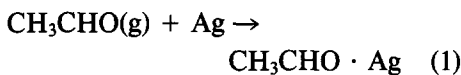
FIG. 8. Response of CH_3COOH caused by the O_2 pulse.

is formed, giving rise to the induction period.

3.4. Active Sites for the Formation of Ethyl Alcohol and Acetic Acid

To clarify the active sites to form CH_3COOH and C_2H_5OH by the reaction of the intermediates with H_2 , the hydrogenation of acetaldehyde is carried out on two different surfaces, reduced and partly oxidized surfaces.

Hydrogenation on reduced surface. On a surface completely reduced with H_2 at $160^\circ C$, the hydrogenation of CH_3CHO steadily proceeds producing C_2H_5OH with no acetic acid and no ethyl acetate. Based on analysis of the data from the transient state and steady state, the following mechanism for the hydrogenation may be presented



The rate can be expressed as

$$r_{EOH} = kP_{H_2} \frac{KP_{CHO}}{1 + KP_{CHO}} \quad (3)$$

The plot of $P_{CHO}P_H/r_{EOH}$ vs P_{CHO} gives a good straight line, and from the slope and the intercept on the axis of the line k and K are estimated

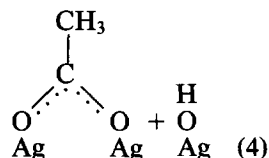
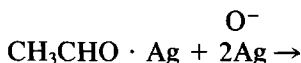
$$k = 4.4 (\pm 0.1) \times 10^{-7}$$

$$\text{mol/g Ag min} \cdot \text{atm.}$$

$$K = 116 (\pm 10) \text{ atm}^{-1}$$

When the partial pressure of CH_3CHO is 0.01 atm, the surface coverage of adsorbed acetaldehyde can be estimated to be 0.54 by assuming its adsorption equilibrium during the hydrogenation. From the first-order dependence with respect to H_2 , gaseous or weakly adsorbed hydrogen reacts with adsorbed aldehyde. These are consistently supported by the transient behavior of the hydrogenation and the analysis of DRIFT spectra during the reaction. Thus, the active sites for the hydrogenation of CH_3CHO seem to be the bare silver surface. If the analogous explanation to that can be applied to the active sites in the reaction between these intermediates (In) in aldehyde oxidation and H_2 , aldehyde adsorbed on bare silver surface may be considered as one of the species constituting (In).

Hydrogenation on partly oxidized surface. Figure 8 illustrates the application of the pulse technique for the formation of CH_3COOH . After the surface had been completely reduced with H_2 , the H_2 stream was replaced by a pure-He stream and then O_2 was pulsed into the inlet of the reactor to prepare the partly oxidized surface, subsequently the CH_3CHO-H_2-He stream was introduced. The larger the O_2 pulse sizes the larger the amounts of CH_3COOH formed. This result means that adsorbed oxygen is necessary to form CH_3COOH , that is to say, CH_3COOH should be formed on the partly oxidized sites, differing from C_2H_5OH which is formed on the bare silver sites. One possible mechanism may be expressed



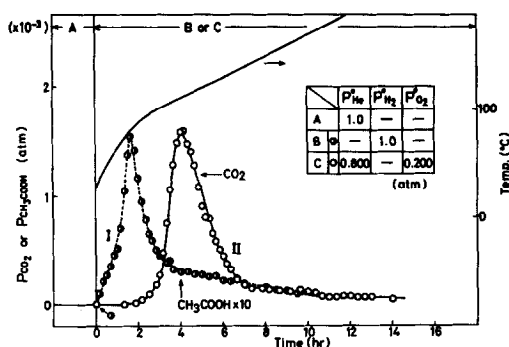
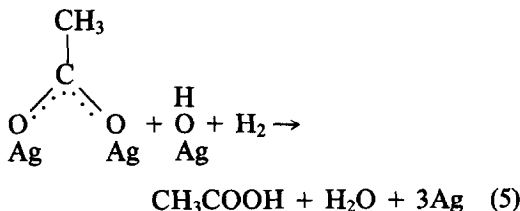


FIG. 9. TPR spectra of the intermediates in H_2 or the O_2 -He mixture.



The same mechanism will be applied to the reaction of (In) with H_2 .

3.5. Similarity of the Intermediates to Solid Silver Acetate

Figures 9 and 10 demonstrate the TPR (Temperature-Programmed Reaction) spectra of the adsorbed intermediates and solid silver acetate, respectively. In both the figures, Spectrum I indicates the formation of CH_3COOH in a pure- H_2 stream, whereas Spectrum II proves the formation of CO_2 and H_2O (H_2O is not presented in the figures) in the O_2 -He (or N_2) stream.

Comparing Spectra I and II in Figs. 9 and

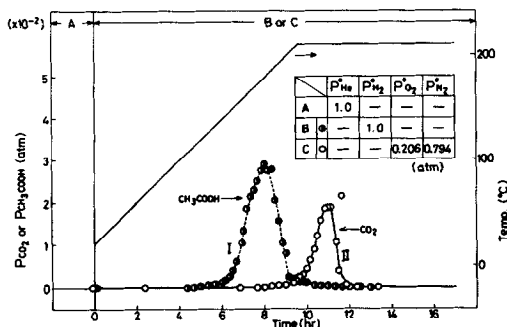


FIG. 10. TPR spectra of solid silver acetate in H_2 or O_2 - N_2 mixture.

10 the formation of CH_3COOH is commonly initiated at lower temperatures than that of CO_2 , suggesting higher reactivity in H_2 than in O_2 . On the other hand, the comparison of TPR spectra between the intermediates and solid silver acetate shows similar behavior, although there is the difference that the intermediates begin to form CH_3COOH and CO_2 at lower temperatures than solid silver acetate. This difference might be caused by the stability of the species existing on the surfaces: the intermediates on silver are more unstable than the surface silver acetate of solid silver acetate. The similarity of the TPR spectra between the two species strongly suggests that one of the intermediates consists of silver acetate. This idea consistently explains all the transient response data on the intermediates formed in the oxidation of acetaldehyde and ethylene oxidation (1-4). Furthermore, the formation of surface silver acetate is confirmed by spectroscopic analysis of the intermediates using FT-IR (DRIFTS), the details of which will be reported later.

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