

Temperature Programmed Reaction Analysis of the Surface Intermediates Formed on Silver in the Oxidation of Acetaldehyde*

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Abstract

Two different transient response techniques, the transient response method and TPR, are applied to analyse the detailed structure of the intermediates which are stably formed on a silver surface in the oxidation of acetaldehyde.

Analysis of the product distribution in the transient response method clearly shows that the intermediates consist of at least three different species: silver acetate form, acetaldehyde form and alcohol form.

The TPR technique newly proposes two additional different species (designated In- α and In- β), in addition to the three species from the transient response method. Both species react with O₂ to produce CO₂ and H₂O, whereas they do not react with H₂. In the TPR spectra in the O₂ stream, In- α and In- β give peaks at 115°C and 150°C, respectively, indicating different reactivity.

1. Introduction

A large number of investigators have extensively studied the reaction mechanism of ethylene oxidation on silver, because only silver can heterogeneously catalyse the ethylene epoxidation.¹⁻⁴⁾ This specific character has aroused these investigators' interest for a long time. One of the most interesting subjects in this reaction are the surface intermediates in the reaction sequences.⁵⁻⁷⁾ As has generally been understood, the reaction consists of parallel consecutive reaction passes: a parallel reaction sequence from ethylene to produce ethylene oxide and carbon dioxide, and a consecutive reaction sequence to produce CO₂ passing through the intermediate product C₂H₄O. For both of the reaction passes, two different ideas have been proposed: one claims a common intermediate for the formation of CO₂ and C₂H₄O and the other claims different intermediates.

Based on the experimental results reported so far in our studies,⁸⁻¹⁰⁾ some stable intermediates are formed on the surface during the reaction. The intermediates react with O₂ producing CO₂ and H₂O, not ethylene oxide, clearly meaning the intermediates produce CO₂. They are accumulated on the surface

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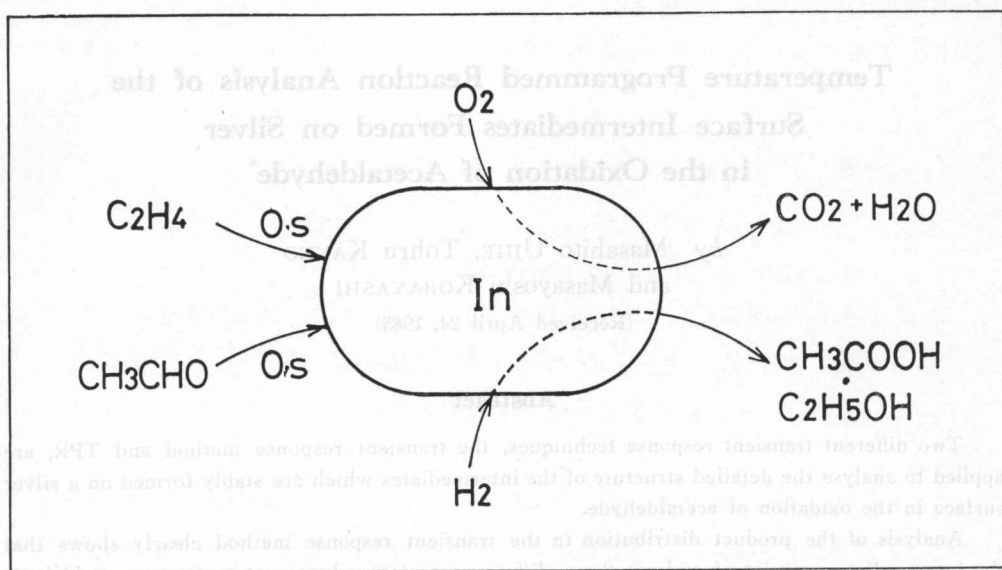


Fig. 1. Simplified reaction mechanism for C_2H_4 and CH_3CHO oxidations.

at temperatures below $110^\circ C$, and their surface coverage falls in the range from $\theta=0.06$ to 0.43 depending on the concentration of C_2H_4 and O_2 . The intermediates exhibit characteristic reactivity and nature: (1) they react with O_2 to produce equal amounts of CO_2 and H_2O , and (2) they react with H_2 to produce acetic acid. A schematic explanation of these reaction is presented in Fig. 1.

In our separate experiments, it has been found that acetaldehyde oxidation on the same silver catalyst can easily proceed to produce CO_2 and H_2O .¹²⁻¹⁷ In the reaction, quite similar intermediates to those of ethylene oxidation are formed on the surface in a temperature range from $110^\circ C$ to $230^\circ C$. The amount of the intermediates formed is two times or one hundred times larger than that in ethylene oxidation at the same temperatures. The greatest difficulties in detecting and analysing the intermediates are their extremely small amounts and the rather small surface area below $1\text{ m}^2/\text{g-Ag}$.^{5,6} Here, one can see an advantage in the large surface amounts of the intermediates present in the case of acetaldehyde oxidation. Thus the oxidation of acetaldehyde may usefully be used to follow the transient behavior of the intermediates during the reaction instead of employing ethylene oxidation.

In the present study, two different unsteady state techniques are used to analyse the adsorbed intermediates: the transient response method and the temperature programmed reaction technique. Two particular subjects, the effect of the intermediates formed in the oxidation of acetaldehyde on the ethylene oxidation and the reactivity of the intermediates, are studied in detail by using the transient response method.¹⁸⁻²⁰ Applying the TPR technique, the detailed reactivity of the intermediates can be visualized by changing the gas components in

the gas phase. The TPR spectra will be able to clearly propose some available information on the different surface species.

2. Experimental Method

2-1. Preparation of the Catalyst

The catalyst is prepared by a conventional procedure to produce the alumina supported silver catalyst for ethylene oxidation. Silver oxide is prepared from silver nitrate solution. A small amount of K_2SO_4 is added as a promoter and a stabilizer for the catalytic activity. Ag_2O and K_2SO_4 are mixed well with a pure grade ethyl alcohol, making a pasty black sample. This is coated on $\alpha-Al_2O_3$ of 20~42 mesh and dried in a dark room for 24 hrs at room temperature. The sample is packed in a reactor and reduced with a H_2 stream at $50^\circ C$ for 12 hrs and then at $100^\circ C$ for 12 hrs. The composition of the catalyst prepared thus is 35.0 wt% -Ag, 0.2 wt% - K_2SO_4 /64.8 wt% - Al_2O_3 and BET surface area is $0.3 \text{ m}^2/\text{g-Ag}$.⁷⁾

2-2. Transient Response Method

The reactor used in this study consists of a Pyrex glass tube 163 cm in length and 0.8 cm inner diameter, in which 262.2 g of catalyst is packed. The reactor is immersed into an oil bath which is excellently controlled within $\pm 0.5^\circ C$ of the desired temperature. O_2 , N_2 , He and H_2 are provided from commercial gas cylinders, and acetaldehyde is fed by passing it through He in liquid acetaldehyde which is kept at $0^\circ C$ by an ice-water bath.

The total gas flow rate commonly used was 160 ± 2 NTP ml/min in all experiments. Three flow control systems were prepared, and each of them could make a different gas composition with the same flow rate. The total flow rate was carefully adjusted so as to equalize the pressure drop between the outlet of the reactor and the outlet of the by-pass stream. One of the three streams was introduced into the reactor and the other two were led to the by-pass outlets. The stream was switched over one of the two by-pass streams to change the gas composition without changing the flow rate, by the use of two four way valves which were attached between the three streams. The residence time of the gas in the reactor was 17 sec and the gas mixing effect was within 5 sec, thereby providing no effect on the transient response curve.

The gas analysis to follow the transient response was conducted by using three gas chromatographs each of which was controlled at different conditions, different column packing, different column length and different bath temperatures, to follow the response curves as continuously as possible. A molecular sieve column was used for the analysis of O_2 and H_2 , and a Porapak Q column was used for CO_2 . For the analysis of CH_3CHO , C_2H_5OH and CH_3COOH , a Porapak R column attached to a FID-gaschromatograph was used.

2-3. TPR Procedure

The reactor and flow control systems used are the same as those for the tran-

sient response method. The programmed temperature is manually operated by changing the electric current of two pipe heaters which are immersed in an oil bath. As is generally seen, the oil bath has a large heat capacity and thereby the temperature change is quite slow. Although the temperature profiles obtained by this procedure shift slightly from an ideally programmed temperature profile, a reproducible locus of temperature increase is obtained in all experiments.

Before starting the TPR experiments, the oxidation of acetaldehyde is conducted with the gas composition of CH_3CHO (1.6%)– O_2 (20.5%)– N_2 (78.9%) for 1 hr at the given temperatures, and thus the reaction intermediates can be formed on the silver surface. After this, the temperature is decreased to room temperature in the He stream for about 2 hrs. Four different TPR schedules are then separately operated as shown schematically in Fig. 2: (1) TPR [H]: the He stream is changed into the H_2 stream at room temperature, and the temperature of the catalyst bed is linearly increased under the scheduled temperature. (2) TPR [O]: the He stream is switched over to the O_2 stream at room temperature, and the temperature is increased. This is not shown in the figure. (3) TPR [HO]: after the TPR [H] experiment, the temperature is decreased to room temperature in H_2 . Then, the He-flush is carried out for 30 min and the He stream is changed into the O_2 stream. The temperature is then increased. And (4) TPR [HO]: after the TPR [O] experiment, the temperature is decreased to room temperature in O_2 . The O_2 stream is switched over to the He stream for a 2 min-flushing of the catalyst bed and then the H_2 stream is introduced. The temperature is then increased. This is not shown in the figure.

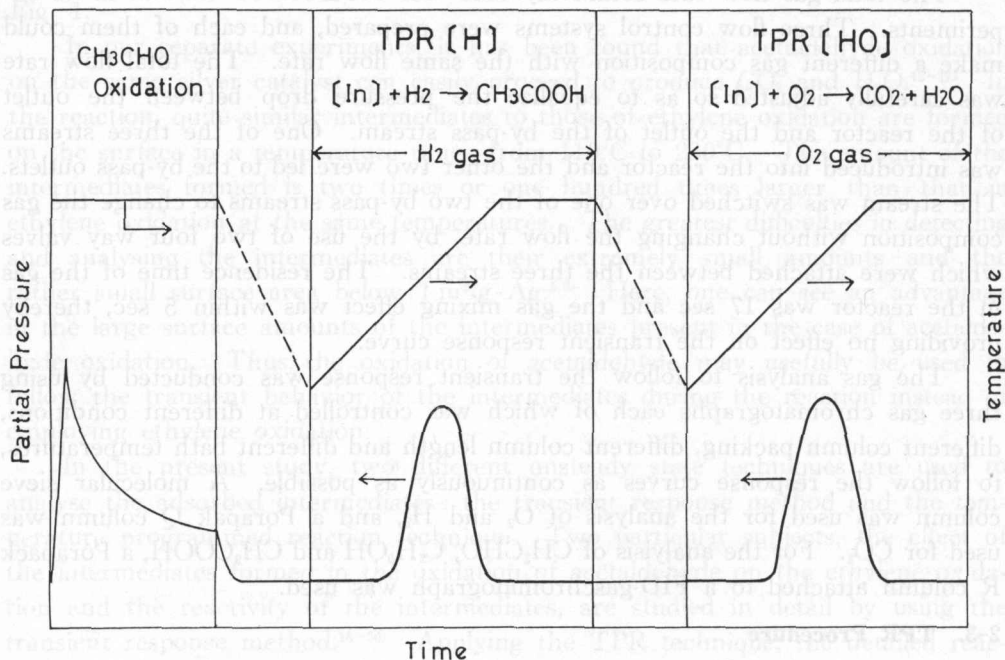


Fig. 2. Schematic explanation for the TPR experiment.

3. Results and Discussion

3-1. Transient Behavior of the Intermediates under Ethylene Oxidation

Fig. 3 shows the transient behavior of CO_2 and $\text{C}_2\text{H}_4\text{O}$ when the reaction gas stream is directly switched from acetaldehyde oxidation to ethylene oxidation. This switching between two different reaction gas streams always gives excellent reproducibility reaching the same reaction steady state value, with no observation of activity decay. As can be seen from the figure, an extraordinarily long induction period of about 10 min is observed which depends on the steady state value of CO_2 in acetaldehyde oxidation, and in some cases, the induction time can be longer than one hour.

To explain why the induction period appears, one may speculate that there are some intermediates on the surface which have been formed during the oxida-

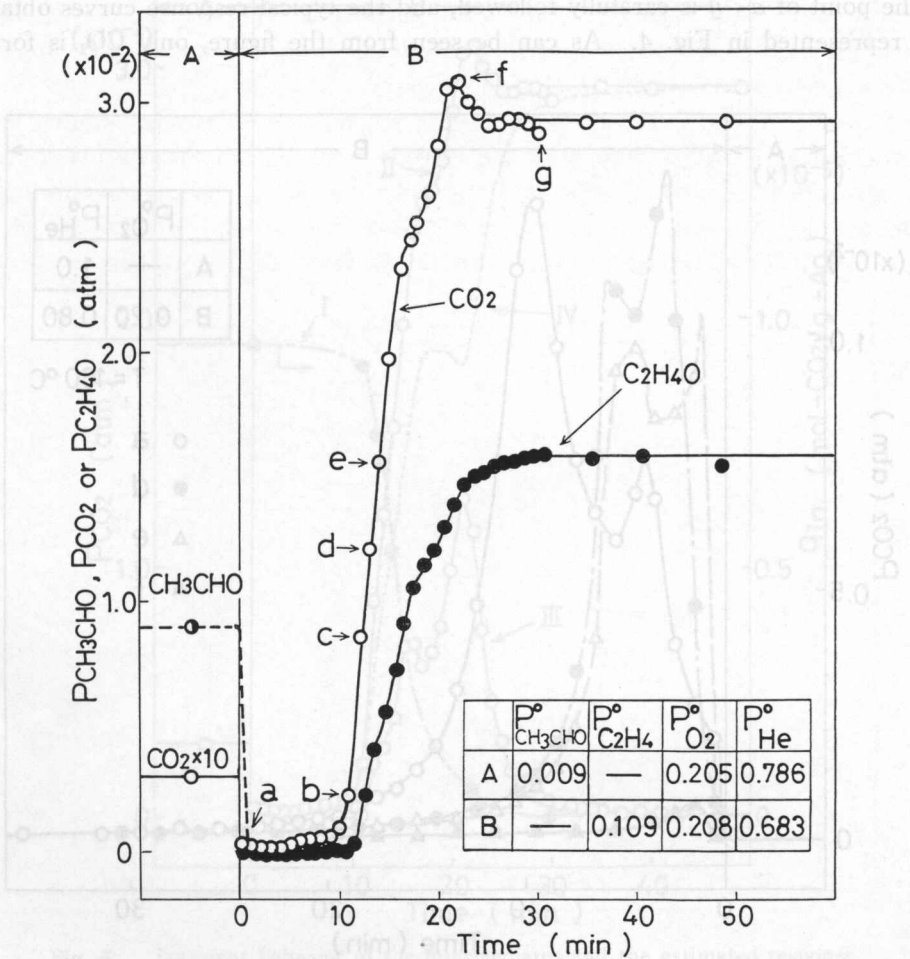


Fig. 3. Transient behavior of CO_2 and $\text{C}_2\text{H}_4\text{O}$ in switching from CH_3CHO oxidation to C_2H_4 oxidation.

tion of acetaldehyde. To speculate further, the amount of the intermediates should occupy most of the surface active sites, and thereby other species could not adsorb on the surface. To confirm the validity of this idea the following experiments are carried out.

To produce the same amount of the adsorbed intermediates in every experiment, the oxidation of acetaldehyde is always carried out until the specific steady state value of CO_2 -partial pressure obtained in the reaction gas mixture-A of Fig. 3 is reached. Here, the rate of CO_2 formation is very slowly decreased with reaction time, and therefore the CO_2 value depends on the reaction time. After this, the reaction gas stream is stepwisely changed into the C_2H_4 (10.9%)- O_2 (20.8%)-He (68.3%) mixture, and the responses of CO_2 and $\text{C}_2\text{H}_4\text{O}$ are followed. At any elapsed time, the time is marked by $a-g$, the catalyst bed is separately flushed by He for 10 min and the He stream is then switched over to the O_2 (20%)- N_2 (80%) mixture. Each response of the products in the final gas stream at the point of $a-g$ is carefully followed, and the typical response curves obtained are represented in Fig. 4. As can be seen from the figure, only CO_2 is formed

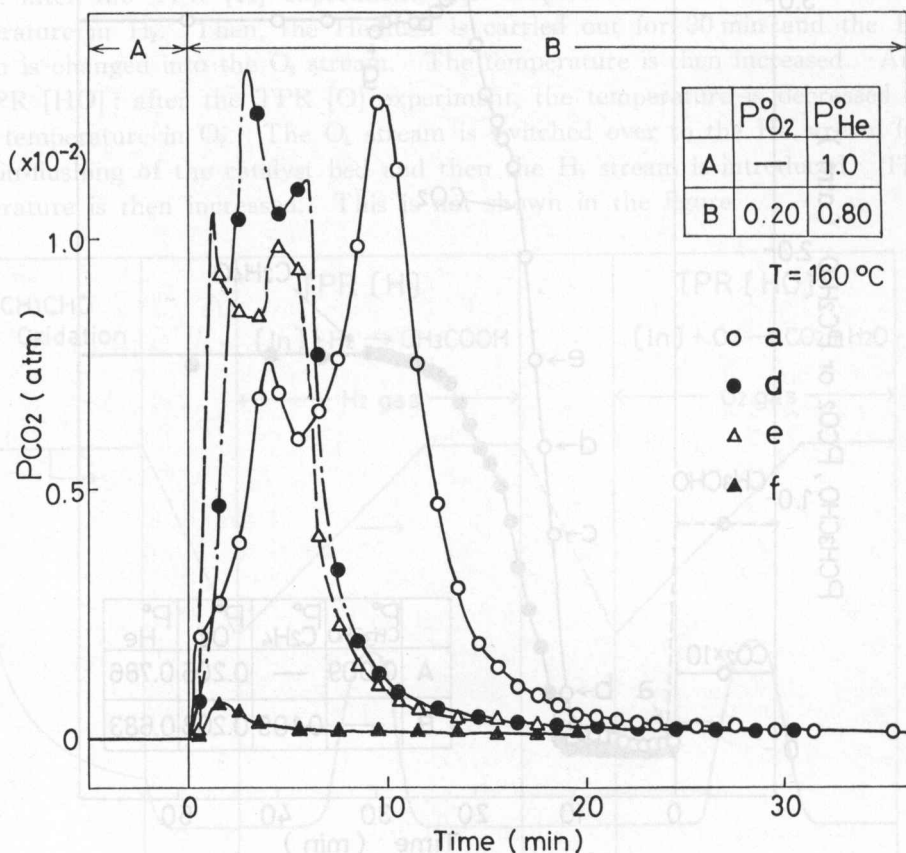


Fig. 4. Decomposition behavior of the intermediates at a point of $a-f$ on the CO_2 -curve in Fig. 3.

with no detection of other products. This CO_2 production should reasonably result from the oxidative decomposition of some intermediates which have mainly been formed during the oxidation of acetaldehyde, with a negligible amount formed in ethylene oxidation.

From the mode of the CO_2 response curves in Fig. 4, one may recognize three characteristics: (1) The amount of the intermediates decreases depending on the elapsed time in the gas mixture of ethylene oxidation, very slowly up to about 10 min of the elapsed time and the rapidly after the induction period (see curve I in Fig. 5). This can be explained by the fact that the intermediates react with the oxygen slowly in the initial stage of the response, because of its rather small fraction of free active sites for the O_2 -adsorption. (2) The initiation time for the decomposition of intermediates becomes faster depending on the

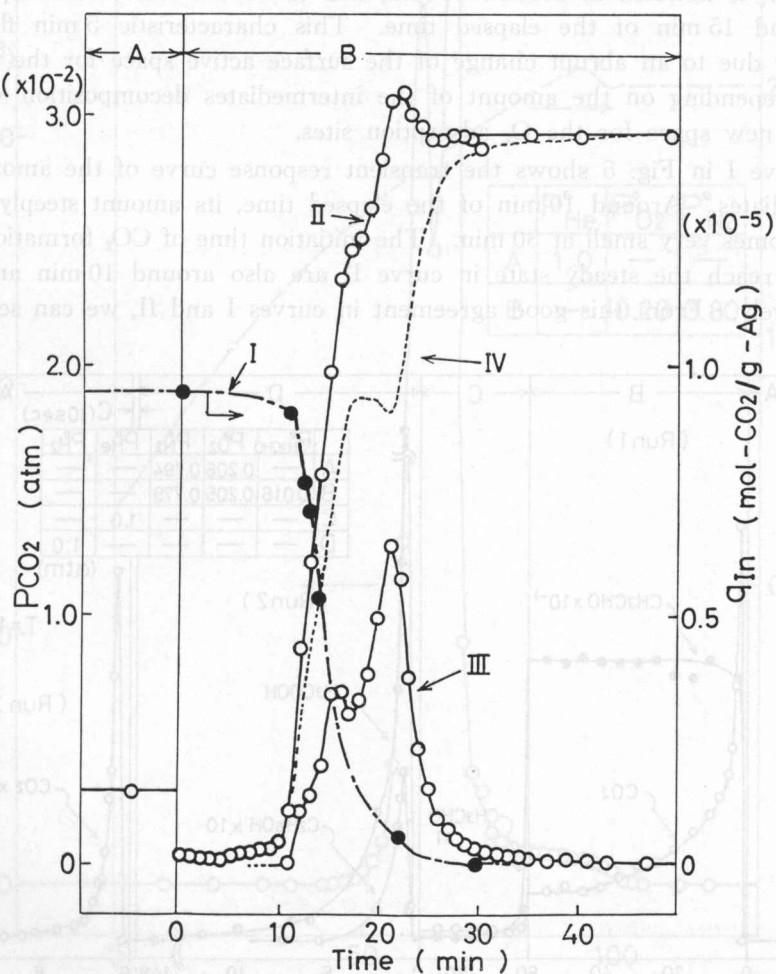


Fig. 5. Transient behavior of the intermediates and the estimated response curve of CO_2 (IV) from the difference between curves II (from CO_2 -curve in Fig. 3) and III (from a curve in Fig. 4).

elapsed time as roughly ordered by *a-f*. This will be illustrated by the increase of the adsorption space for O_2 . And (3) All response curves except curve *f* have two peaks, strongly suggesting the existence of two different adsorbed species with different reactivity.

Redrawing the CO_2 -curve in Fig. 3 into Fig. 5, one can interpret curve II in Fig. 5 as being a curve superposed with two different curves III and IV: curve III shows the response curve of CO_2 formed by the reaction between the intermediates and oxygen, and curve IV indicates a curve of CO_2 formed by the ethylene oxidation on the active sites free from the intermediate adsorption. Curve IV, therefore, is drawn from the difference between curves II and III. Here, curve III is separately obtained by exposing the intermediates to the O_2-N_2 mixture. Analysing curve IV in detail, the complete oxidation of ethylene to form CO_2 is initiated at around 10 min, and the curve has a flat step of 5 min at around 15 min of the elapsed time. This characteristic 5 min flat step is probably due to an abrupt change of the surface active space for the adsorption of O_2 , depending on the amount of the intermediates decomposition which will make a new space for the O_2 adsorption sites.

Curve I in Fig. 5 shows the transient response curve of the amount of the intermediates. Around 10 min of the elapsed time, its amount steeply decreases and becomes very small at 30 min. The initiation time of CO_2 formation and the time to reach the steady state in curve II are also around 10 min and 30 min, respectively. From this good agreement in curves I and II, we can see that the

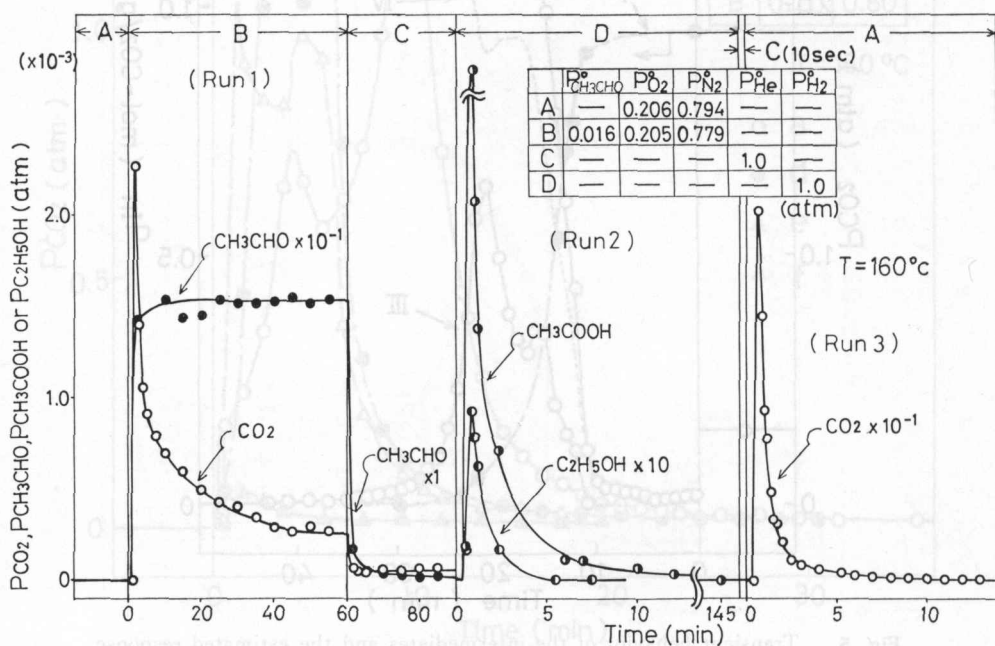


Fig. 6. Transient reactivity of the intermediates formed in the oxidation of CH_3CHO .

accumulation of the intermediates on the surface is caused by the long induction period to initiate the ethylene oxidation. The extensive surface occupation by the intermediates thus inhibits the progress of ethylene oxidation. The results strongly suggest that the active sites in the oxidation of acetaldehyde are the same as those in the oxidation of ethylene. Based on this idea, to clarify the structure and nature of the intermediates it should reasonably be important to study the reaction mechanism of ethylene oxidation.

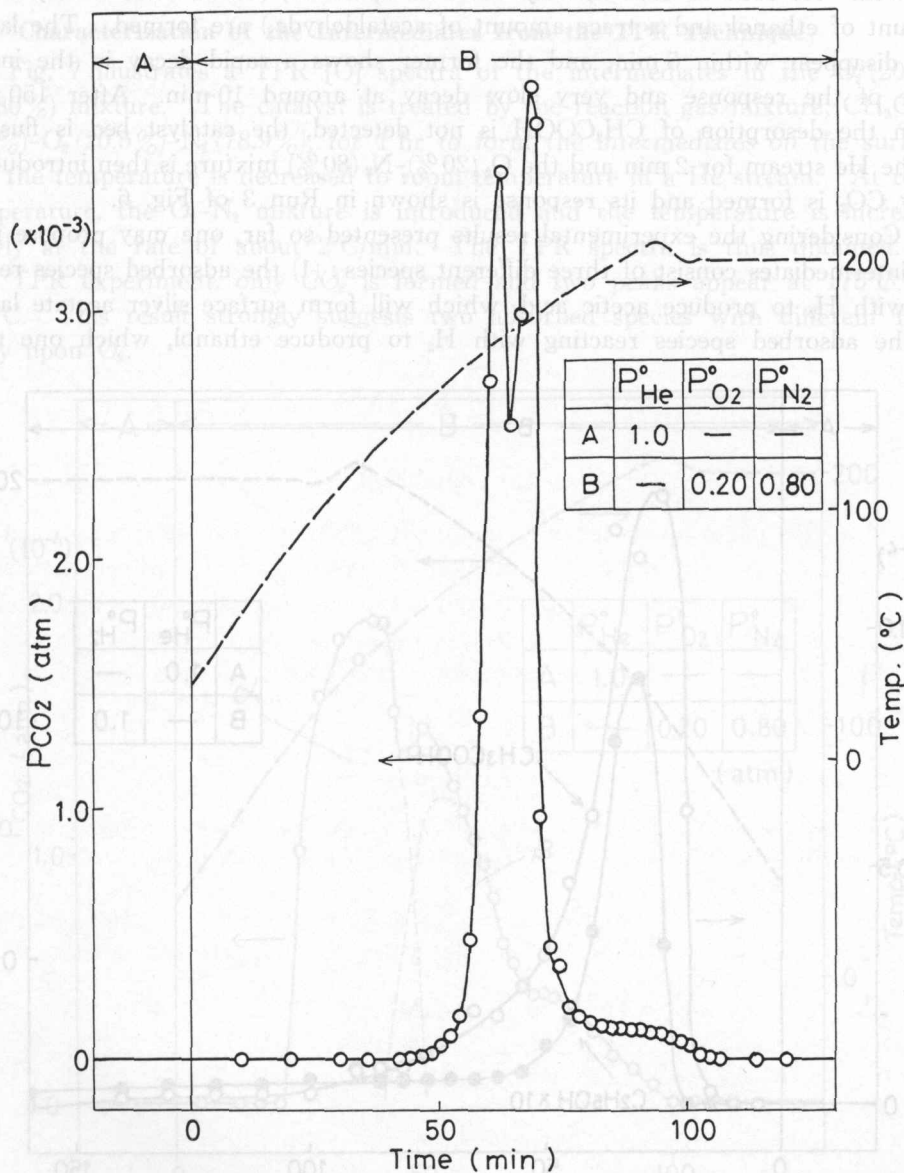


Fig. 7. TPR [O] spectrum of the intermediates formed at 160°C.

3-2. Transient Reactivity of the Intermediates in H_2 and O_2

Fig. 6 illustrates the reactivity of the intermediates under the transient state. In Run 1, the oxidation of acetaldehyde has been carried out for 60 min with the reaction gas mixture, CH_3CHO (1.6%)– O_2 (20.5%)– N_2 (78.9%), at $160^\circ C$. When the desorption of acetaldehyde approaches to zero, then the catalyst bed is flushed by the He stream for 30 min. In Run 2, the He stream is switched over to the H_2 stream, and the responses of the products in the outlet stream are carefully followed. As seen in Run 2, only three components, (acetic acid, a very small amount of ethanol and a trace amount of acetaldehyde,) are formed. The latter two disappear within 5 min, and the former shows a rapid decay in the initial stage of the response and very slow decay at around 10 min. After 150 min when the desorption of CH_3COOH is not detected, the catalyst bed is flushed by the He stream for 2 min and the O_2 (20%)– N_2 (80%) mixture is then introduced. Only CO_2 is formed and its response is shown in Run 3 of Fig. 6.

Considering the experimental results presented so far, one may propose that the intermediates consist of three different species: (1) the adsorbed species reacting with H_2 to produce acetic acid, which will form surface silver acetate layer, (2) the adsorbed species reacting with H_2 to produce ethanol, which one may

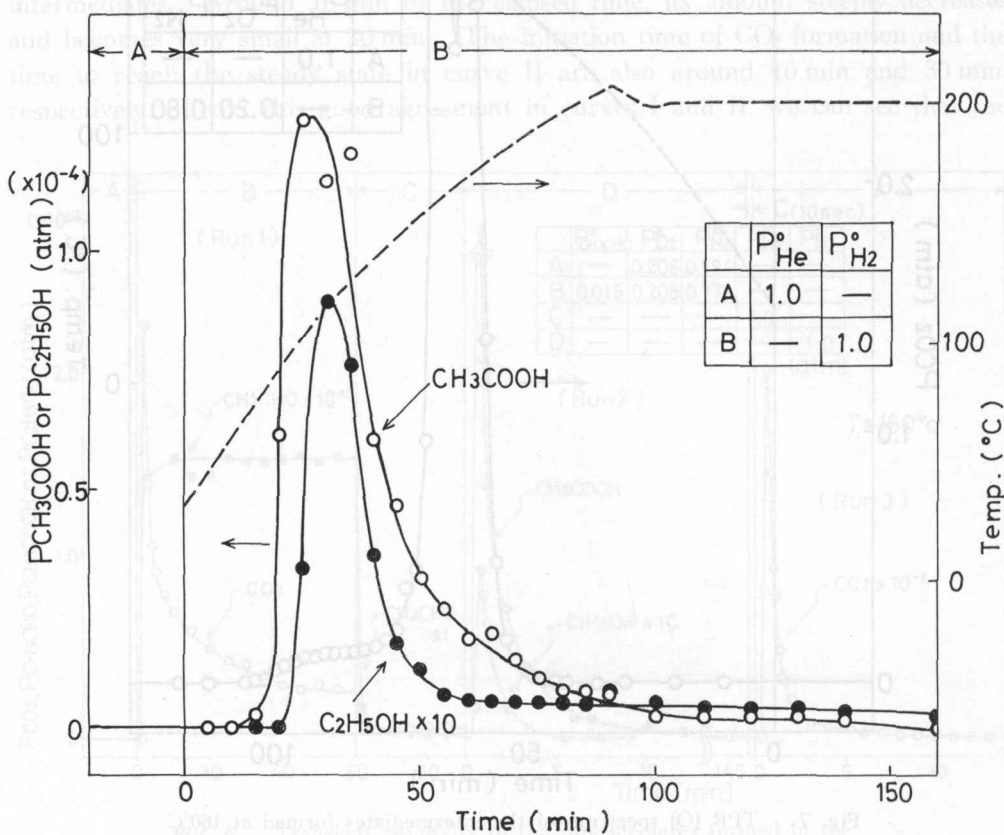


Fig. 8. TPR [H] spectra of the intermediates formed at $160^\circ C$.

speculate to be strongly adsorbed acetaldehyde and (3) the adsorbed species to desorb as acetaldehyde, which will be weakly adsorbed acetaldehyde.

Noting Run 3 in Fig. 6, the formation of CO_2 strongly suggests the existence of some additional intermediates which have no reactivity with H_2 , because the intermediates are stably retained during Run 2 with no reaction. This is quite interesting evidence for other new species in addition to the three species detected in the H_2 stream. The nature of these species will be discussed in detail in the next section.

3-3. Characterization of the Intermediates from the TPR Technique

Fig. 7 illustrates a TPR [O] spectra of the intermediates in the O_2 (20%)– N_2 (80%) mixture. The catalyst is treated by the reaction gas mixture, CH_3CHO (1.6%)– O_2 (20.5%)– N_2 (78.9%), for 1 hr to form the intermediates on the surface, and the temperature is decreased to room temperature in a He stream. At room temperature, the O_2 – N_2 mixture is introduced and the temperature is increased slowly at the rate of about $2^\circ\text{C}/\text{min}$. The TPR spectra is thus obtained. In this TPR experiment, only CO_2 is formed and two peaks appear at 175°C and 185°C . This result strongly suggests two adsorbed species with different reactivity upon O_2 .

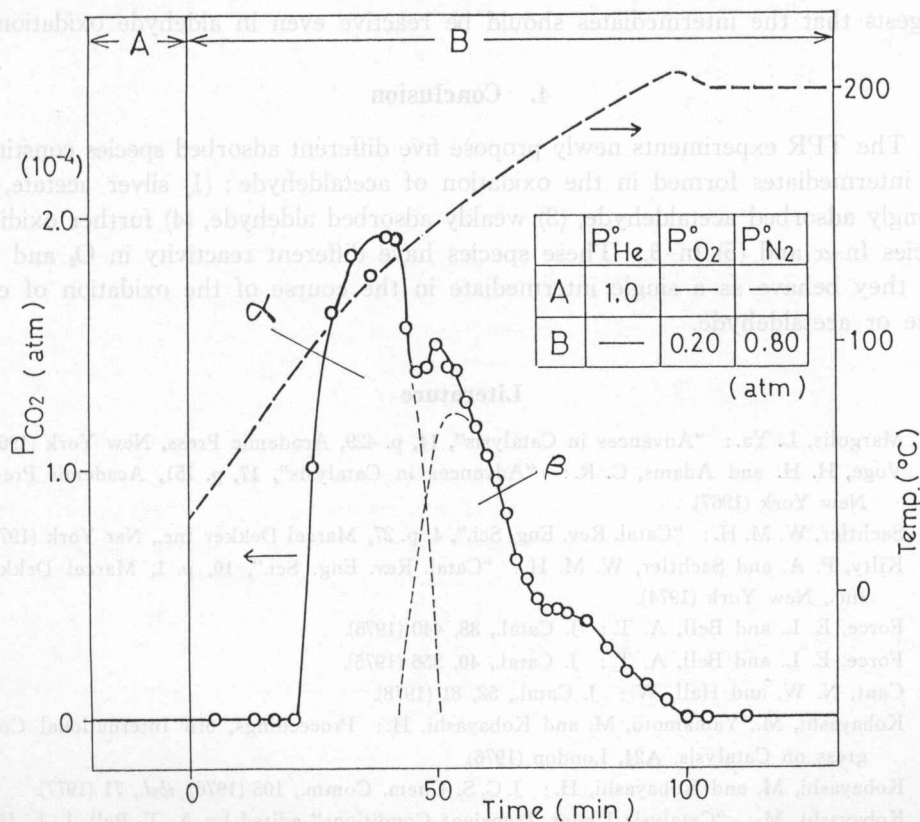


Fig. 9. TPR [HO] spectrum of the intermediates formed at 160°C .

Fig. 8 indicates a TPR [H] spectra in the H_2 stream. In this case, mainly CH_3COOH , a very small amount of C_2H_5OH and a trace amount of acetaldehyde (which is not shown in the figure) are formed. The spectra of CH_3COOH and C_2H_5OH commonly give a peak temperature of about $130^\circ C$, which is lower than the case of CO_2 in the $O_2(20\%)-N_2(80\%)$ stream presented above. From this difference between the O_2 and H_2 streams, one may recognize that the intermediates are more reactive with H_2 than with O_2 .

Fig. 9 shows a TPR [HO] spectrum. As can be seen from the figure, only CO_2 is formed with no other products. One can recognize two peaks in the spectrum at $115^\circ C$ and $150^\circ C$, again suggesting that the intermediates consist of two additional different adsorbed species to the three species which were previously detected in the TPR [H] experiment. Here, the former with the peak temperature of $115^\circ C$ and the latter with $150^\circ C$ are named as In- α and In- β , respectively. This TPR [HO] spectrum may be understood as the superposed spectra of two spectrum shown by dotted curves in the figure. The graphical integration of the two spectrum evaluates as 2.2×10^{-7} mol/g-Ag (In- α) and 1.9×10^{-7} mol/g-Ag (In- β). The initiation temperatures to decompose in- α and In- β are $90^\circ C$ and $130^\circ C$, respectively. In addition, their peak temperatures are also lower than the reaction temperatures of acetaldehyde oxidation, $150^\circ C \sim 230^\circ C$. This evidence strongly suggests that the intermediates should be reactive even in aldehyde oxidation.

4. Conclusion

The TPR experiments newly propose five different adsorbed species constitute the intermediates formed in the oxidation of acetaldehyde: (1) silver acetate, (2) strongly adsorbed acetaldehyde, (3) weakly adsorbed aldehyde, (4) further oxidized species In- α and (5) In- β . These species have different reactivity in O_2 and H_2 , and they behave as a single intermediate in the course of the oxidation of ethylene or acetaldehyde.

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1. Introduction

It has been pointed out, in general, it is not easy to clearly detect the intermediates on silver in the oxidation of ethylene at industrial reaction rates. For that reason, one may find that there is little adsorption because of the small reacting surface area, and the difficulty of IR transmission in the solid samples using the traditional transmission technique.^{1,2,3}

In our previous papers, we showed that when the oxidation of ethylene is carried out at low pressure below 110°C, some stable adsorbed intermediates are formed in large quantities on the surface, which were confirmed to be the intermediates in the oxidation of ethylene.^{4,5,6} It was also confirmed that the same intermediates are formed on the surface during the oxidation of acetaldehyde. One advantage is that the amounts are from two to a hundred times larger than those in ethylene oxidation. A new in-situ tool for the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was developed and effectively used to analyze such intermediates, and the typical spectra obtained

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