

Fine Structure of the Temperature Programmed Reaction Spectra of Silver Acetate Visualized by a Mass Spectrometer

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Abstract

The Temperature Programmed Reaction (TPR) spectra of solid silver acetate were finely visualized by using a mass spectrometer assisted by a personal computer. The TPR spectra obtained exhibited only two products, CO_2 and CH_3COOH . The population and the TPR spectra-pattern of the two products were sensitively affected by the rate of temperature rise and the gas atmosphere, in O_2 , He or H_2 , indicating the different reaction mechanisms depending on the gas phase components. CH_3COOH was mainly produced in H_2 whereas CO_2 and CH_3COOH were commonly produced in O_2 or He. For the formation of CO_2 four different reaction intermediates were presumed, whereas for the formation of CH_3COOH in O_2 , He and H_2 , two reaction paths would be presumed to supply active hydrogen for the hydrogenation of silver acetate. The activation energy to form CO_2 was evaluated to be 32 ± 4 kcal/mol in He, which shifted extremely depending on the gas atmosphere.

1. Introduction

Ethylene oxidation over silver is a typical complex reaction of triangular type; the direct formation of CO_2 from C_2H_4 and the consecutive formation of CO_2 via $\text{C}_2\text{H}_4\text{O}$ as an intermediate product. The detailed reaction mechanisms for the formation of the two products have not been clarified sufficiently.¹⁻⁶⁾ So far, many surface intermediates have been proposed for the two products and some of them have been identified by using the tracer⁷⁻¹⁰⁾ or the spectroscopic technique, especially the in-situ infrared spectroscopic technique.^{11,12)} On the formation of $\text{C}_2\text{H}_4\text{O}$, the adsorbed intermediate is difficult to detect during the reaction, because the desorption rate of $\text{C}_2\text{H}_4\text{O}$ is fast and the much smaller amount adsorbed on the surface leads us to the further difficulty of its detection on the surface by the spectroscopic technique.

For the formation of CO_2 , on the other hand, several intermediates have undoubtedly been detected on silver surface. Force and Bell^{11,12)} proposed a

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mechanism to form CO_2 , via three species, acetate ($\text{H}_3\text{C}-\text{C}(\text{H})-\text{O}-\text{Ag}$), oxalate ($\text{O}=\text{C}-\text{C}(\text{O})-\text{Ag}$)

and $\text{CH}_3\text{COOH}\cdot\text{Ag}$ -species presumed as precursors. Barteau, Bowker and Madix¹³⁾ studied in detail the reactions of CH_3COOH and CH_3CHO with adsorbed oxygen by using a temperature programmed desorption technique. They proposed a stable acetate type intermediate for the adsorption of CH_3COOH , and $\text{CH}_3\text{CHO}_2(\text{ad})$ for the adsorption of CH_3CHO which could be converted into the stable acetate by heating. The acetate intermediate was further converted into CO_2 , CH_3COOH , CH_4 and $\text{H}_2\text{C}=\text{C}=\text{O}$. In our previous papers,¹⁴⁻²³⁾ the reaction intermediates in complete oxidations, ethylene oxidation and acetaldehyde oxidation, were examined and found to have in good similarity in their nature and adsorbed structure. Three different adsorbed species were proposed as composing the intermediates: the silver acetate form intermediate (CH_3COOAg) which produced CH_3COOH in H_2 and CO_2 and H_2O in O_2 , the strongly adsorbed acetaldehyde which produced $\text{C}_2\text{H}_5\text{OH}$ in H_2 and CO_2 and H_2O in O_2 , and the weakly adsorbed acetaldehyde which easily desorbed in He.

Based on the above experimental results, it can be seen that there are several kinds of intermediates on the surface for the complete oxidation of C_2H_4 . Our recent studies further support the presence of the silver acetate species (CH_3COOAg) during the reaction using two techniques, an in-situ diffuse reflectance infrared fourier transform spectroscopic technique^{20,22-25)} and a temperature programmed reaction technique.^{22,27)} On the detailed reactivity of the intermediates, additional two different species were proposed: the new species give further two peaks of the TPR spectrum of CO_2 formation in the O_2 stream, which were obtained after the TPR experiments in the H_2 stream.

Our interest is thus focused on the acetate type intermediate (CH_3COOAg) which should be one of the important intermediates for the complete oxidation of C_2H_4 . In the present study, solid silver acetate has been studied in detail by using the temperature programmed reaction/decomposition (TPR/TPD) technique, as a model species for the intermediates.

The intermediates consist of some kinds of species to be decomposed into CO_2 and H_2O via several kinds of intermediates which have more oxidized forms. Each intermediate should give its own characteristic TPR/TPD spectra accompanying a complex spectrum with many peaks and with narrow spectra bands. In our previous works,^{23,25,27)} the complex spectrum could not be distinguished because of the analytical limitations of the gas-chromatograph which was too slow to analyse rapid TPR responses. The aim of this study is to analyse the fine structure of the TPR/TPD spectra of solid silver acetate relating to the adsorbed intermediates in ethylene oxidation, and to distinguish the mixed reaction intermediates, by using a mass spectrometer assisted by a personal computer.

2. Experimental Procedure

The solid silver acetate (SSA) used in this study was supplied from Wako Pure Chemical Co. without further purification. 0.5 g of fine powdered SSA was packed in a Pyrex glass tube reactor (0.7 cm inner diameter and 85 cm length). A chromel-alumel thermocouple of 1 mm ϕ was inserted into the white powder sample bed which was 5 cm high. The flow diagram of the experimental equipment is presented in Fig. 1. The reactor was immersed in a sand fluidized bath, the temperature of which was finely controlled by a programmed temperature controller (CHINO JP-1131) with an accuracy of $\pm 0.5^\circ\text{C}$ at the desired temperatures. Three different heating rates, 1°C , 2°C and $4^\circ\text{C}/\text{min}$, were chosen for the TPR/TPD experiments.

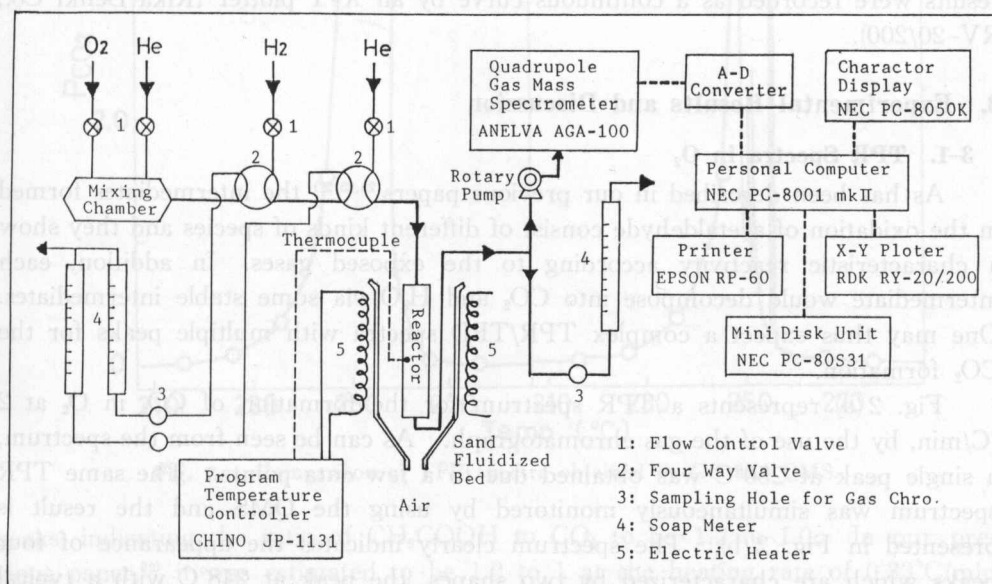


Fig. 1. Schematic diagram of apparatus for the TPR/TPD methods.

Oxygen (O_2 , 99.99%; N_2 , 0.0047%), helium (He , 99.999%; O_2 , 0.0009%), and hydrogen (H_2 , 99.995%) were provided from commercial gas cylinders with no further purification. The total gas flow rate was kept constant at 160 ± 1.3 ml(NTP)/min, and the mean residence time of the gas was at most about 0.36 sec. Three flow control systems were prepared and they were connected with two four way valves between the three for the transient response experiments. The outlet flow from the reactor was divided into two pathways; one was the main flow (130 ml(NTP)/min) which was led to a vent and the other was a small part of the flow (30 ml(NTP)/min) which was introduced into a mass spectrometer by using a rotary vacuum pump.

Two gas chromatographs (GC) and a quadrupole mass spectrometer (QMS) were simultaneously used to follow the TPR/TPD responses. The gas chroma-

tograph attached to FID was used to analyse the hydrocarbons formed (CH_3COOH , $\text{C}_2\text{H}_5\text{OH}$, etc.) by the use of a Porapak R column, and the GC with TCD was used for the analysis of CO , H_2 , O_2 and CO_2 by a molecular sieve 5 A and a Porapak Q columns. The QMS was scanned from one to a hundred amu by the repetition in the period of three seconds. The monitored mass numbers were 44 amu for CO_2 , 43/60 amu for CH_3COOH and 32/16 amu for O_2 . Each intensity of the mass number was converted into digital signals by using an A/D converter, and the signals were accumulated in a personal computer (NEC, PC-8001 mkII). The PC-8001 could simultaneously collect the signals for fourteen different kinds of mass number at intervals of ten seconds, and these data were accumulated on a mini floppy disk. The stored data were automatically converted into the partial pressure of each component by the computer, and the final results were recorded as a continuous curve by an X-Y plotter (Rika Denki Co., RV-20/200).

3. Experimental Results and Discussion

3-1. TPR Spectra in O_2

As has been described in our previous papers,^{23,25,27} the intermediates formed in the oxidation of acetaldehyde consist of different kinds of species and they show a characteristic reactivity according to the exposed gases. In addition, each intermediate would decompose into CO_2 and H_2O via some stable intermediates. One may thus expect a complex TPR/TPD spectra with multiple peaks for the CO_2 formation.

Fig. 2(a) represents a TPR spectrum for the formation of CO_2 in O_2 at 2 °C/min, by the use of the gas chromatograph. As can be seen from the spectrum, a single peak at 250°C was obtained due to a few data points. The same TPR spectrum was simultaneously monitored by using the QMS and the result is presented in Fig. 2(b). The spectrum clearly indicates the appearance of four peaks which are characterized by two shapes, the peak at 248°C with a typical symmetric shape and the other three peaks at 251, 252 and 256°C with a steep shape and a narrow width, differing from the TPR spectrum by the GC technique. This complex spectrum is confirmed to be reproducible by the repetition of the same experiment. From the result, it would be reasonable to presume that four stable reaction intermediates were formed in the course of the reaction of SSA with O_2 . They will have different oxidized forms and decomposition rates.

The graphical integration of the spectra of CO_2 at 248 (α -peak), 251 (β -peak), 252 (δ -peak) and 256°C (γ -peak) in Fig. 2(b) represents the amounts of each peak 3.1×10^{-3} , 7.9×10^{-5} , 1.0×10^{-4} and 3.2×10^{-4} mol/g-Ag, respectively. The population of α , β , γ and δ peaks are evaluated to be 86.0, 2.2, 2.8 and 9.0%, respectively. Fig. 3 illustrates the TPR spectra superposed for both CO_2 and CH_3COOH in O_2 . The spectrum of CH_3COOH gives a broad peak. The integrated amount of CH_3COOH formed was calculated to be 4.3×10^{-3} mol/g-Ag. This amount is fairly close to the total amounts of CO_2 (3.6×10^{-3}) summed on α - δ

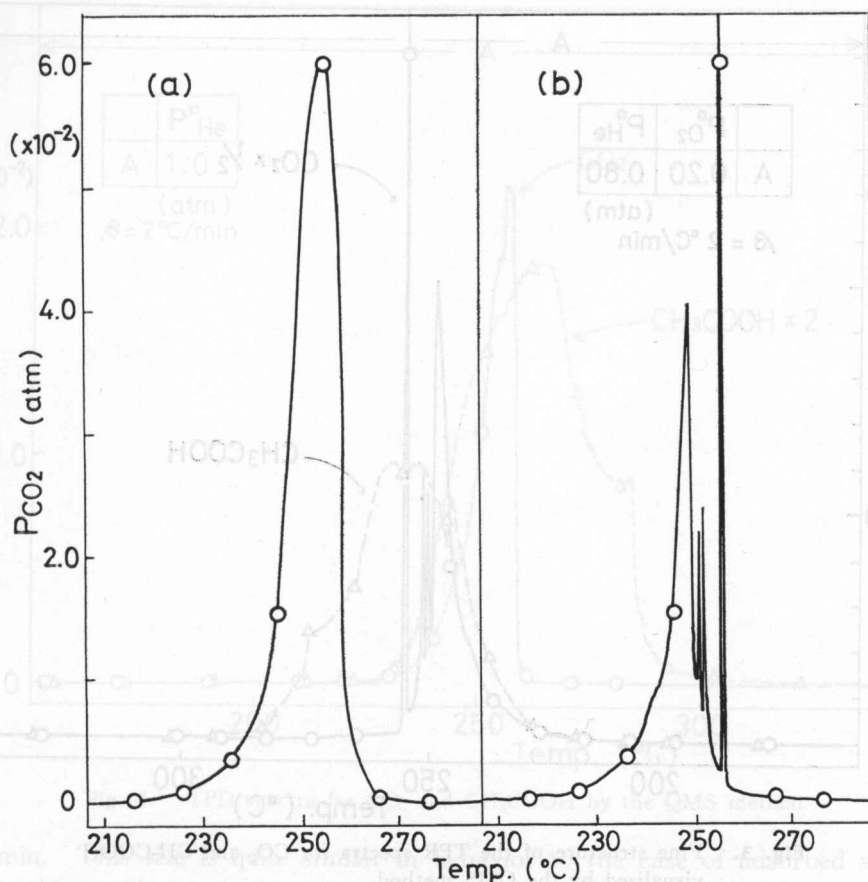
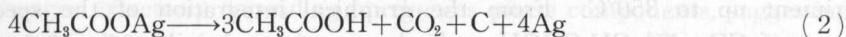


Fig. 2. Comparison of TPR spectra obtained by GC and QMS.

peaks, indicating the ratio of CH_3COOH to CO_2 to be 1.2 to 1.0. In our previous paper,²²⁾ it was estimated to be 1.2 to 1 at the heating rate of $0.33^\circ\text{C}/\text{min}$ by using GC data. Based on this good reproducibility and taking into account the discussions by early workers²⁸⁻³⁰⁾, one may again speculate the following two reactions, regardless of the change of heating rate, 2 and $0.33^\circ\text{C}/\text{min}$.



When equations (1) and (2) simultaneously occur, the ratio of CH_3COOH to CO_2 should become 1:1 which is very close to the obtained experimental value. Let us speculate a simple model to explain the four peaks. Peak α might result from the desorption of carboxylate fragments formed from the decomposition of CH_3COOAg , and peaks β , γ and δ would result from the reactive carbon formed from CH_3 -fragments. The amount of the latter three are sensitively changed by the heating rate, suggesting that the reactive carbon is seriously affected by the heating rate.

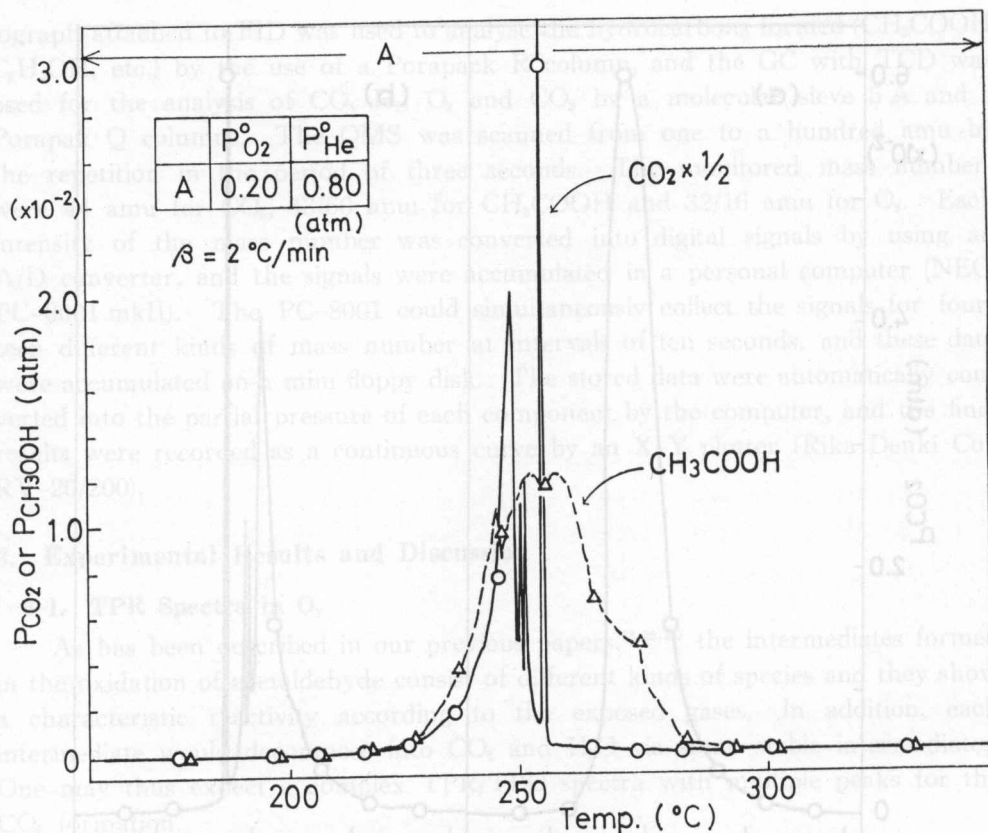


Fig. 3. Fine structure of the TPR spectra for CO_2 and CH_3COOH visualized by the QMS method.

The separate TPR experiments on the intermediates in acetaldehyde oxidation clearly confirm the appearance of α - δ peaks. This similarity again leads us to the conclusion that the reactivity of solid silver acetate is analogous with the intermediates in acetaldehyde oxidation.

3-2. TPD Spectra in He

Fig. 4 illustrates the temperature programmed decomposition (TPD) spectra in He at 2°C/min . Only two products were detected in the course of the TPD experiment up to 350°C . From the graphical integration of the spectra, the amounts of CO_2 and CH_3COOH evolved are estimated to be 2.3×10^{-3} and 3.4×10^{-3} mol/g-Ag, respectively. The decomposition conversion is estimated to be 48.9% from the carbon balance. One may recognize the formation of carbonaceous materials in the sample from its dark gray color, resulting from the oxygen-deficiency in the gas phase. This is the reason why the carbon balance is low.

Fig. 5 illustrates the TPD spectra in He for CO_2 formation at the different rates of temperature rise, 1°C , 2°C and 4°C/min . As can be seen from the comparison between the three spectra, the peak temperature is raised higher by raising the heating rate, as 244°C at 1°C/min , 256°C at 2°C/min and 264°C at

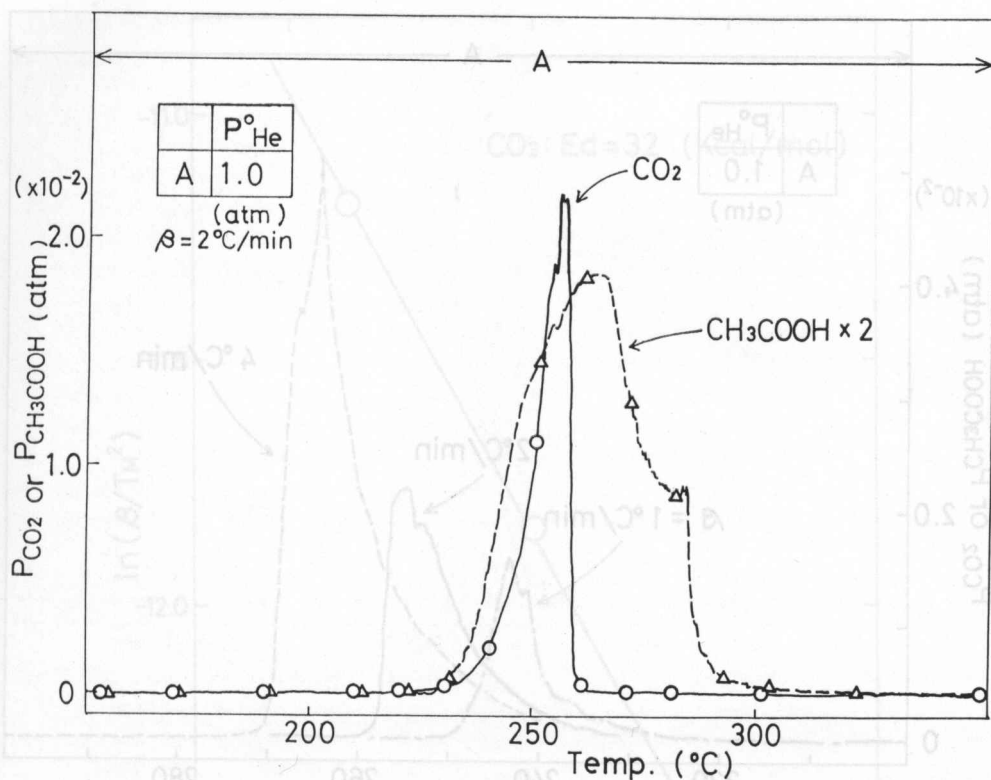


Fig. 4. TPD spectra for CO_2 and CH_3COOH by the QMS method.

4°C/min . This rise is quite similar in behavior to the case of adsorbed species. From this similarity, it may be possible to use the following equation which is usually employed for the adsorbed species.³¹⁾

$$\ln(\beta/T_m^2) = -E_d/R \times 1/T_m - \ln C \quad (3)$$

Where, β , E_d , T_m and C are heating rate ($^\circ\text{C/min}$), activation energy for the decomposition (kcal), peak temperature (K) and constant, respectively. Fig. 6 illustrates the plots of $\ln(\beta/T_m^2)$ vs $1/T_m$ and the result clearly shows a good straight line. From the slope of the straight line, the activation energy for the decomposition of SSA in He is estimated to be 32 ± 4 kcal/mol. This activation energy changes extremely depending on the gas phase components, suggesting the change in rate determining steps or reaction mechanism. The detailed results will be reported later.

Noting the shape of the CH_3COOH -spectrum in Figs. 3 and 4, one may recognize the presence of two peaks and the similarity between them in O_2 and in He. This similarity would suggest a closed mechanism between the two different gas phase components. One possible explanation for the appearance of the two peaks is the change in the rate determining steps to supply the active hydrogen. The first higher peak of the spectrum is caused by the rate controlling step to be the formation of active hydrogen from the thermal decompo-

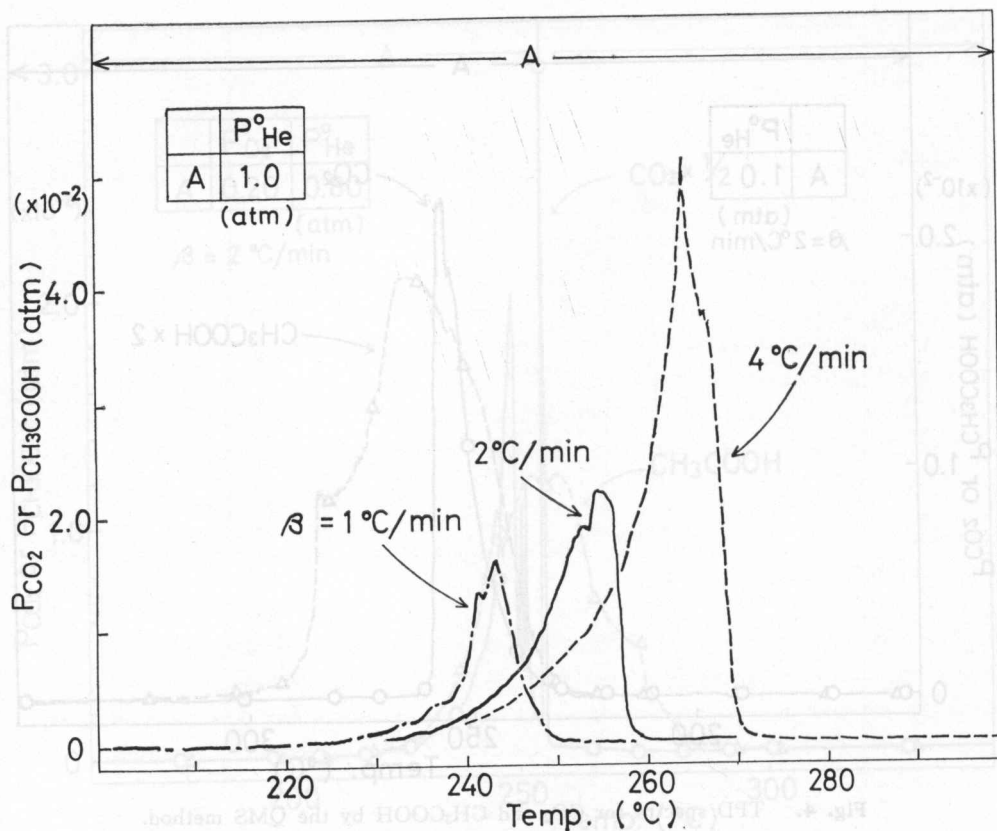


Fig. 5. Variation of the TPD spectra for CO_2 with changing the heating rate.

sition of solid silver acetate. The second lower peak is caused by the rate controlling step to be the supplying of the active hydrogen from localized parts in solid silver acetate. The broad shape would be due to the slow desorption of CH_3COOH from silver metal formed.

3-3. TPR Spectra in H_2

Fig. 7 illustrates the TPR spectra in H_2 . The graphical integration of the spectra shows the amounts of CH_3COOH and CO_2 to be 5.7×10^{-3} mol/g-Ag and 9.7×10^{-5} mol/g-Ag, respectively. The ratio of CH_3COOH and CO_2 is 59:1 which is a value quite close to the previous results, (60:1),²² even though showing spectra of quite a different shape and a different heating rate. The total conversion is 62.1%, much lower than the previous one (96%). It has separately been confirmed that the conversion is drastically decreased depending on the heating rate in the region of $0.1 \sim 2^\circ\text{C}/\text{min}$. Speculation falls on the slow diffusion rate of H_2 into bulk silver acetate compared to the rate of thermal decomposition. In the present case, one may again propose the simultaneous reaction sequences of two reactions, (2) and (4) in parallel,

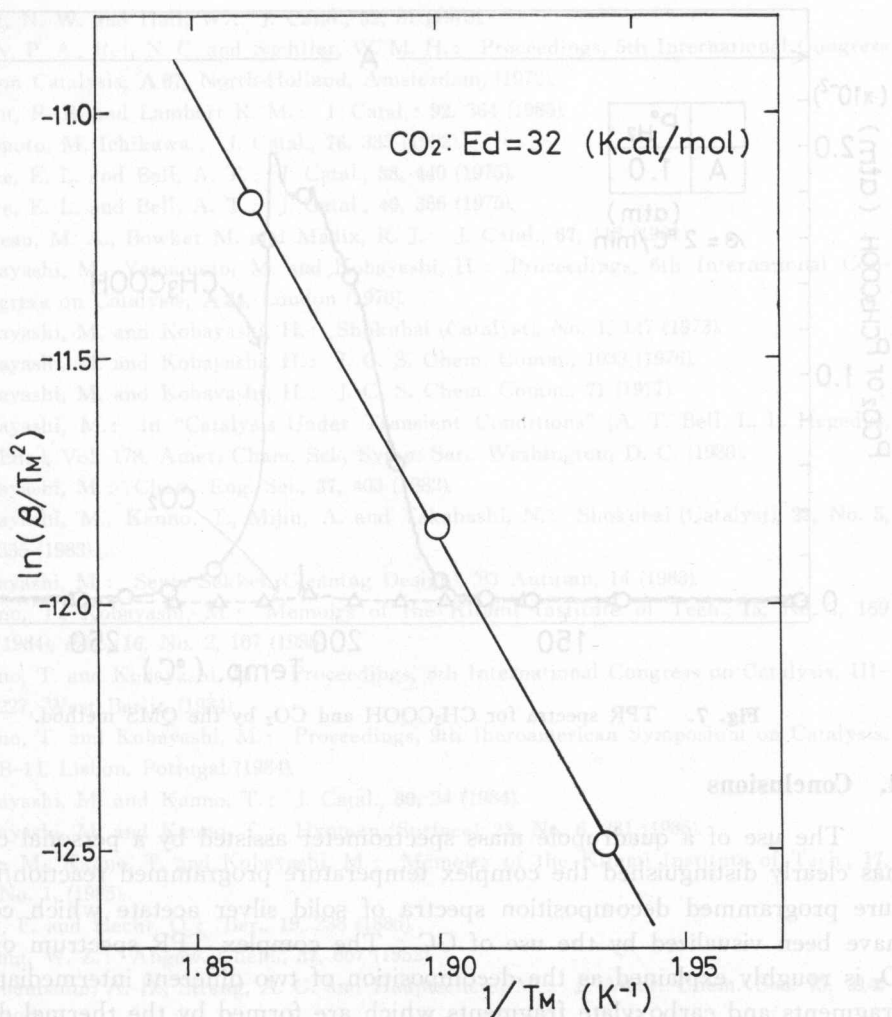
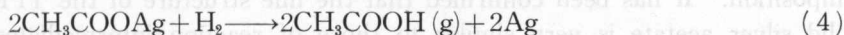


Fig. 6. Plots of $\ln(\beta/T_m^2)$ vs. $1/T_m$ based on equation (3).



Noting the shape of the TPR spectra of CH_3COOH in Fig. 7 compared to the TPR/TPD spectra of CH_3COOH in Fig. 3 or 4, the peak temperature is shifted from 216°C to 255°C or 264°C , and the shape of the spectrum gives one peak whereas CH_3COOH in Figs. 3 and 4 indicates two peaks. Although it is difficult to clarify the reason for this difference, one may speculate that, in the case of that in H_2 , active hydrogen to react with solid silver acetate is easily supplied from gaseous H_2 . In O_2 or He , on the other hand, the active hydrogen would be only supplied from the thermal decomposition of solid silver acetate which partially occurred in the course of TPR/TPD.

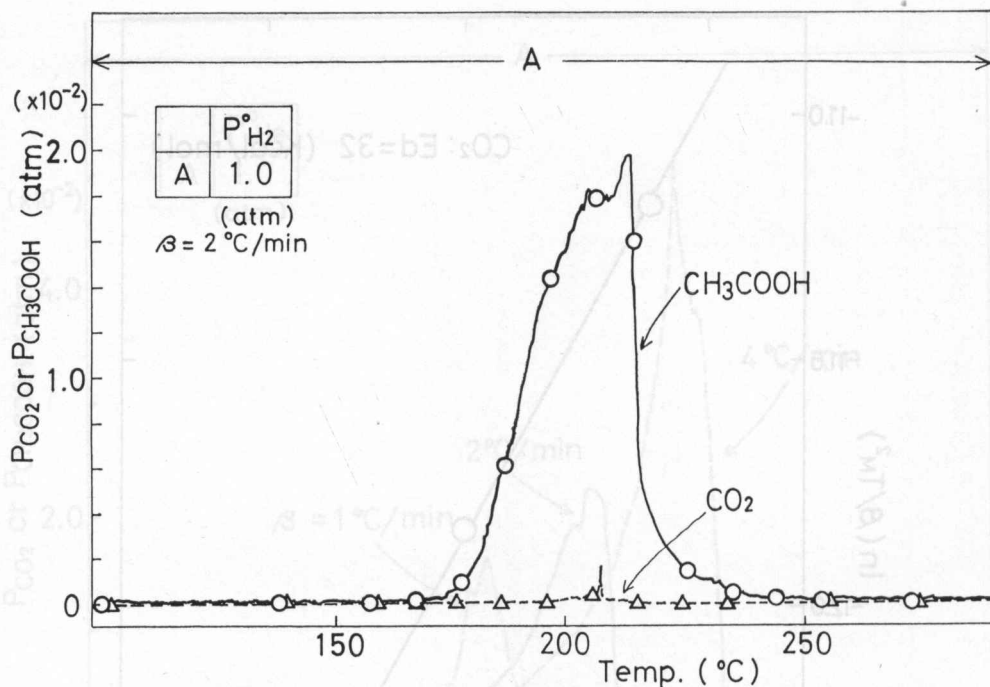


Fig. 7. TPR spectra for CH_3COOH and CO_2 by the QMS method.

4. Conclusions

The use of a quadrupole mass spectrometer assisted by a personal computer has clearly distinguished the complex temperature programmed reaction/temperature programmed decomposition spectra of solid silver acetate which could not have been visualized by the use of GC. The complex TPR spectrum of CO_2 in O_2 is roughly explained as the decomposition of two different intermediates, CH_3 -fragments and carboxylate fragments which are formed by the thermal decomposition of CH_3COOAg and converted into four intermediates by their successive decomposition. It has been confirmed that the fine structure of the TPR spectra of solid silver acetate is very similar to those of reaction intermediates in acetaldehyde oxidation, suggesting the similarity of their decomposition mechanisms.

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1. ま え が き

今般、日本のエネルギー源の大部分は石油に依存し、そのほぼ全量を輸入しているが、将来にわたる石油事情を考えると、石油代替エネルギーの開発は急務である。現在、代替燃料である石炭が注目されつつあるが、その燃焼特性は純炭質の炭では優れているが、実