Transient Reactivity of Solid Silver Acetate in Hydrogen and Oxygen by In Situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy*

by Tohru Kanno and Masayoshi Kobayashi

Department of Industrial Chemistry, Kitami Institute
of Technology, 090 Kitami, Hokkaido, Japan

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Abstract

The reactivity of solid silver acetate in hydrogen and oxygen has been studied by using the transient response method and the in situ diffuse reflectance infrared fourier transform spectroscopic (DRIFTS) technique to compare its nature to that of the reaction intermediates in ethylene oxidation. On the analysis of the transient response curves, solid silver acetate produced acetic acid and a small amount of carbon dioxide in a hydrogen stream, and produced CO_2 and a small amount of CH_3COOH in an oxygen stream. Temperature programed reaction (TPR) spectra of the two products commonly exhibited a peak temperature of 170°C in the hydrogen stream and 210°C in the oxygen stream, indicating that its reactivity in the hydrogen stream should be higher than in the oxygen stream. A possible reaction mechanism has been proposed for both streams.

A new IR cell has been developed for the in situ DRIFTS study under transient states, and it was confirmed that the response of the cell to the step change in gas composition was within two seconds. The transient responses of the characteristic absorption bands for the surface species of solid silver acetate, in the H_2 stream or in the O_2 stream, are in good agreement with those from the transient response method.

1. Introduction

In our previous papers[1~8], it has been demonstrated that there are some stable intermediates in the complete oxidation of ethylene over a silver catalyst, when the reaction is operated at temperatures lower than 130°C. The reaction model can be visualized as

$$C_2H_4 \xrightarrow{\quad O^- \quad} In \text{ (intermediates)} \xrightarrow{\quad O_2^- \quad} CO_2, H_2O \qquad (1)$$
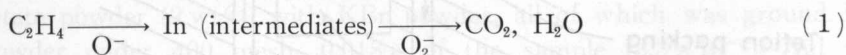
where O^- and O_2^- are monoatomic surface oxygen species and diatomic surface oxygen species, respectively. The nature and the reactivity of one of the intermediates is quite similar to silver acetate including its infrared spectra. As our first approach to clarify the structure of the intermediate, it may reasonably be proposed that the intermediate should have a similar structure to silver acetate. From this stand point, the nature and the reactivity of solid silver acetate can be compared to those of the intermediate to relate both structures. In the present

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study, the characteristic reactivity of solid silver acetate has been extensively studied by using the transient response method and the diffuse reflectance infrared spectroscopic technique.

A new in situ infrared cell has been developed to accurately follow the transient response of infrared absorption bands. The new cell for the DRIFTS is extremely useful and convenient for following the transient behavior of solid surface species during the reaction with no affect from gas mixing, and to prepare the sample, which is a fine powder, it is not necessary to make pressed thin disks.

2. Experimental Procedure

Special grade solid silver acetate produced by Wako Pure Chemical Industries Ltd. was employed as a sample for the DRIFTS technique. Two grams of solid silver acetate were packed into four Pyrex glass tubes each of which was connected with a silicon tube, so that the sample in the reactors can be obtained for the DRIFTS technique to follow the surface structure change during the reaction. The reactors were immersed in an oil bath the temperature of which was excellently controlled within $\pm 0.5°C$ at the desired temperatures. The total gas flow rate was 80 cc(NTP)/min. For the transient response method, a further detailed experimental procedure will be found elsewhere.[9~11]

For the in situ DRIFTS technique, a new cell was developed so as not to have any effect on gas mixing in the cell. The old cell used in our previous papers[12,13] was a diffusion type, in which the gas flow passed under a sample
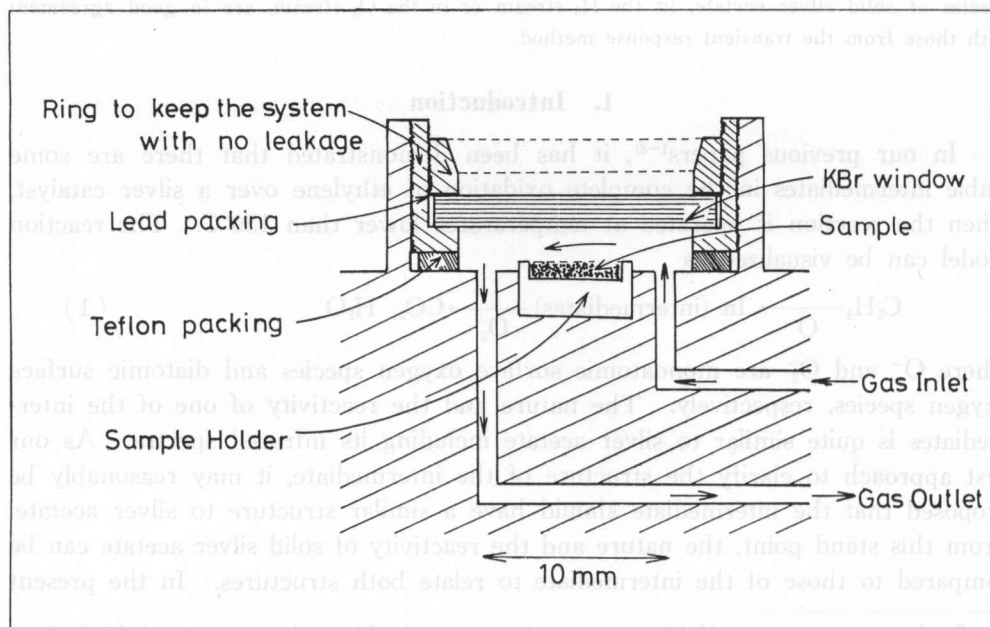

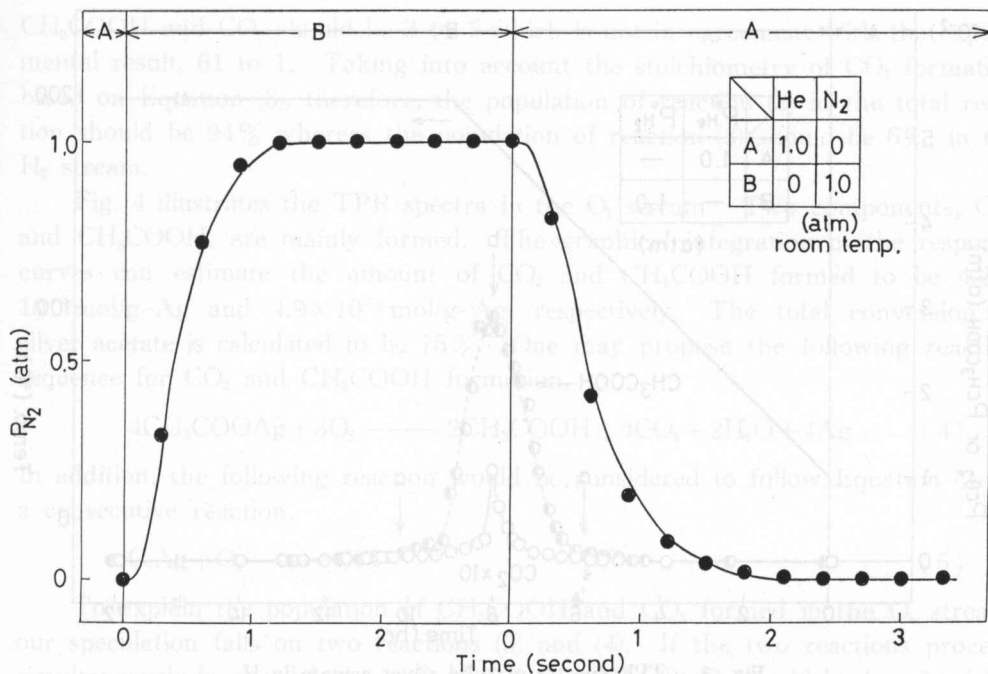Fig. 1. Schematic drawing of the IR cell for the in situ DRIFTS.

Fig. 2.   Transient response of the IR cell in the step change of gas composition between N_2 and He.

holder and the gas contacted the sample by molecular diffusion through four holes in the sample holder. The new cell is carefully constructed so that the gas flow goes as straight as possible, and the schematic structure of the cell is presented in Fig. 1. The gas mxing effect was examined and found to be negligible by the transient response curves between N_2 and He gas flows, using a quadrupole type mass spectrometer to analyse N_2, where the total gas flow rate was 160 cc/min. Typical response curves obtained thus are presented in Fig. 2. As can be seen from the figure, the delay of the response curves is within two seconds, indicating no gas mixing effect in the cell.

The sample for the DRIFTS technique was prepared by mixing the solid silver acetate powder (2 wt%) with KBr powder, all of which was ground into a fine powder under 400 mesh. 0.018 g of the sample [2.3×10^{-4} g-Ag] was placed on a sample holder and the flow rate of gas was 30 cc (NTP)/min.

3.   Experimental Results and Discussion

3-1.   Transient Reactivity of Solid Silver Acetate in H_2 and O_2.

The reactivity of solid silver acetate is extensively examined in the H_2 and O_2 gas streams under elevating temperature and the response of the outlet gas flow is followed by using gas chromatographs as continuously as possible. The response curve obtained thus may be called the temperature programed reaction (TPR) spectra. Fig. 3 is the result in the H_2 stream. The components of the
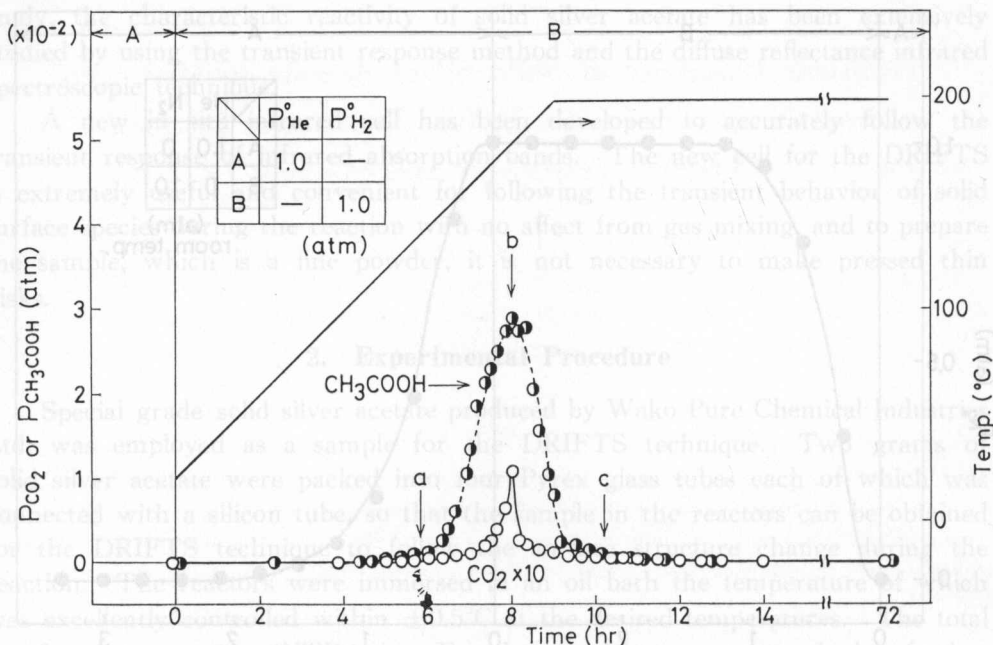
Fig. 3. TPR spectra of solid silver acetate in H_2.

efluent gas stream are confirmed to be mainly acetic acid with a small amount of carbon dioxide. The graphical integration of the TPR spectra obtained gives the total amount of the components to be $8.0(\pm0.2)\times10^{-3}$ mol CH_3COOH/g-Ag and $0.13(\pm0.03)\times10^{-3}$ mol CO_2/g-Ag. Based on the carbon balance, the total conversion of the solid silver acetate used can be calculated to be $90(\pm5)\%$ which changes depending on the degree of water content in the sample. It is difficult to remove all water in the sample because of its unstable structure at high temperatures.

From the experimental result that the color of the sample after the TPR experiment was light gray, one may speculate that the sample had been completely converted into CH_3COOH and CO_2 to produce metallic silver. This metallic silver sample obtained thus is active for the ethylene oxidation. This is also further support for the metallic silver form, because it is experimentally confirmed that solid silver acetate is not active for the oxidation of ethylene, and the activity of silver partly containing solid silver acetate is unstable.

The mechanism for the production of acetic acid in H_2 may be proposed as follows,

$$2CH_3COOAg+H_2\,(g)\longrightarrow 2CH_3COOH\,(g)+2Ag \qquad (2)$$

For the mechanism for CO_2 formation, the following equation has been well known[14~18]

$$4CH_3COOAg\longrightarrow 3CH_3COOH+CO_2+C+4Ag \qquad (3)$$
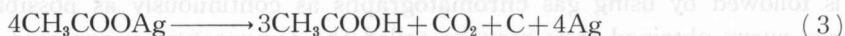
If Equation (3) proceeds in advantage rather than Equation (2), the ratio of

CH_3COOH and CO_2 should be 3 to 1 which is not in agreement with the experimental result, 61 to 1. Taking into account the stoichiometry of CO_2 formation based on Equation (3), therefore, the population of reaction (2) in the total reaction should be 94% whereas the population of reaction (3) should be 6%, in the H_2 stream.

Fig. 4 illustrates the TPR spectra in the O_2 stream. Two components, CO_2 and CH_3COOH, are mainly formed. The graphical integration of the response curves can estimate the amount of CO_2 and CH_3COOH formed to be 4.2×10^{-3} mol/g-Ag and 4.9×10^{-3} mol/g-Ag, respectively. The total conversion of silver acetate is calculated to be 75%. One may propose the following reaction sequence for CO_2 and CH_3COOH formation,

$$4CH_3COOAg + 3O_2 \longrightarrow 2CH_3COOH + 4CO_2 + 2H_2O + 4Ag \qquad (4)$$

In addition, the following reaction would be considered to follow Equation (3) as a consecutive reaction,

$$C.Ag + O_2 \longrightarrow CO_2 \qquad\qquad\qquad\qquad (5)$$

To explain the population of CH_3COOH and CO_2 formed in the O_2 stream, our speculation falls on two reactions (3) and (4). If the two reactions proceed simultaneously in parallel, the ratio of CO_2 and CH_3COOH should be 1 to 1 which is very close to the experimental result, 1 to 1.2. This result strongly suggests that reactions (3) and (4) will proceed in parallel with the population of 1 to 1. The color of the sample after the TPR experiment in the O_2 stream is dark
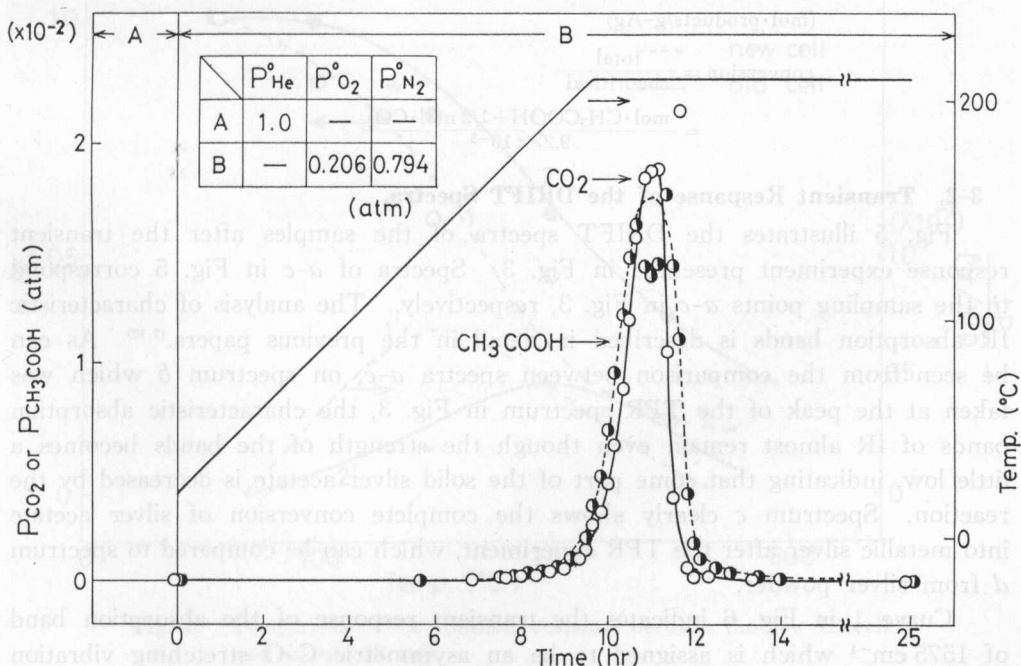

Fig. 4. TPR spectra of solid silver acetate in the O_2–N_2 mixture.

gray. From this evidence one could speculate that some of the carbon in Equation (3) resides in the sample. This is the reason why the total conversion of silver acetate is 75% lower than that in H_2.

Comparing Figs. 3 and 4, one can see that the peak temperature of the TPR spectrum in H_2 is lower than that in O_2. In addition, the starting temperature of reaction with the gaseous components is also lower than that in O_2. These results strongly support our speculation that the reactivity of silver acetate with H_2 is higher than with O_2. The results are summarized in Table 1. Since solid silver acetate is less active in O_2 than in H_2, reaction (4) needs higher activation energy than reaction (2). Reaction (3) in O_2 should partly proceed in advantage compared to that in H_2.

Table 1. Graphical Analysis of TPR spectra in the H_2 or O_2 gas stream

	H_2	O_2
Peak Temp. (°C)	190	210
CH_3COOH ($\times 10^{-3}$)	7.9	4.9
CO_2 ($\times 10^{-3}$)	0.13	4.2
conversion	0.96	0.75

(mol·products/g–Ag)

$$\text{conversion} = \frac{\text{total}}{\text{theoritical}}$$

$$= \frac{\text{mol} \cdot CH_3COOH + 1/2 \ \text{mol} \cdot CO_2}{9.27 \times 10^{-3}}$$

3-2. Transient Response of the DRIFT Spectra.

Fig. 5 illustrates the DRIFT spectra of the samples after the transient response experiment presented in Fig. 3. Spectra of *a–c* in Fig. 5 correspond to the sampling points *a–c* in Fig. 3, respectively. The analysis of characteristic IR absorption bands is described in detail in the previous papers.[12,13] As can be seen from the comparison between spectra *a–c*, on spectrum *b* which was taken at the peak of the TPR spectrum in Fig. 3, the characteristic absorption bands of IR almost remain even though the strength of the bands becomes a little low, indicating that some part of the solid silver acetate is decreased by the reaction. Spectrum *c* clearly shows the complete conversion of silver acetate into metallic silver after the TPR experiment, which can be compared to spectrum *d* from silver powder.

Curve 1 in Fig. 6 indicates the transient response of the absorption band of 1575 cm^{-1} which is assigned to be an asymmetric C–O stretching vibration during the TPR of solid silver acetate, and the temperature schedule used is
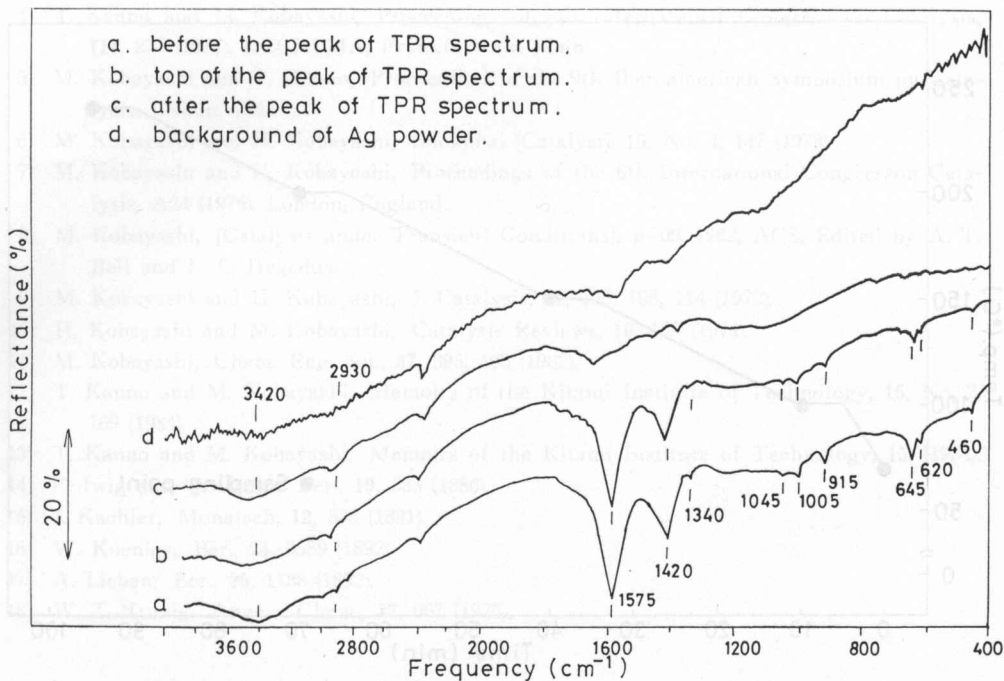
Fig. 5. IR spectra by the DRIFTS for solid silver acetate during the TPR in H_2. a, b, and c respectively correspond to a-c in Fig. 3.
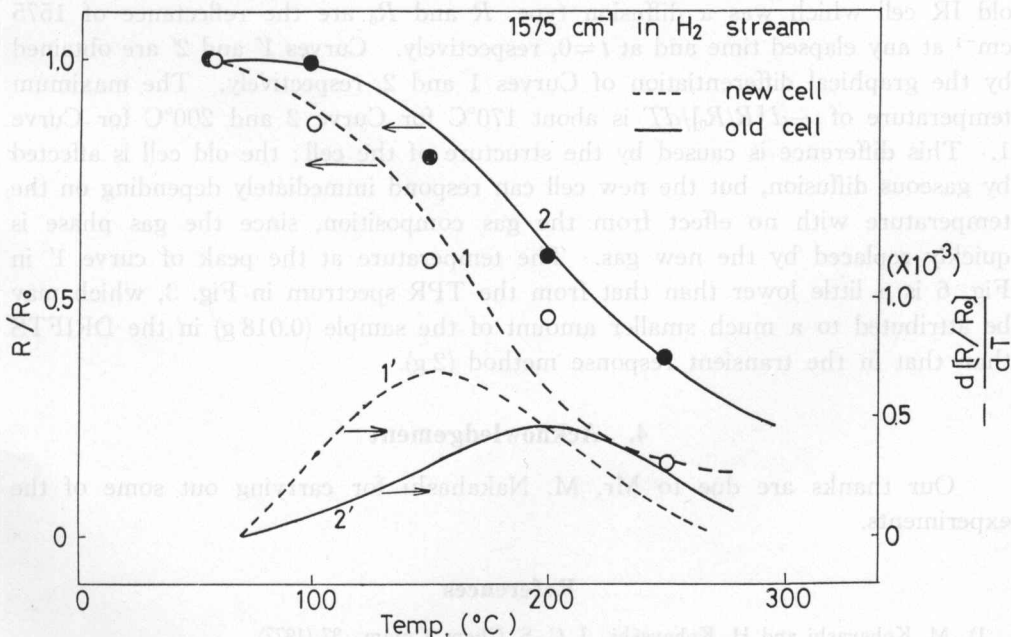

Fig. 6. Comparison of the transient response between the new IR cell and the old IR cell.
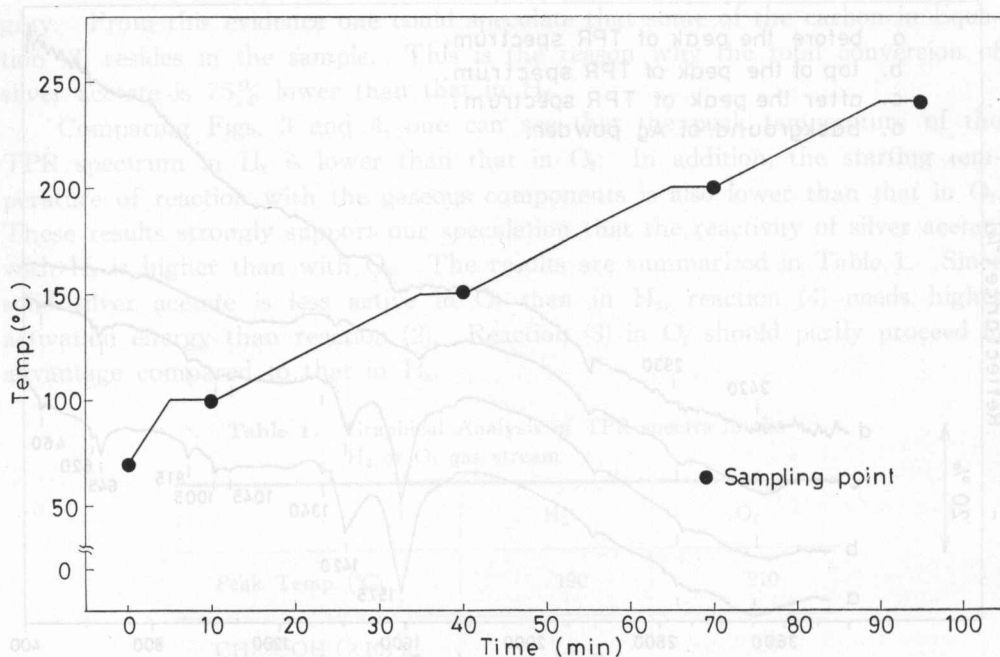
Fig. 7. Temperature schedule for the TPR experiment.

presented in Fig. 7. Curve 2 in Fig. 6 represents the response curve from the old IR cell which was a diffusion type. R and R_0 are the reflectance of 1575 cm^{-1} at any elapsed time and at $t=0$, respectively. Curves 1' and 2' are obtained by the graphical differentiation of Curves 1 and 2, respectively. The maximum temperature of $-d[R/R_0]/dT$ is about 170°C for Curve 2 and 200°C for Curve 1. This difference is caused by the structure of the cell; the old cell is affected by gaseous diffusion, but the new cell can respond immediately depending on the temperature with no effect from the gas composition, since the gas phase is quickly replaced by the new gas. The temperature at the peak of curve 1' in Fig. 6 is a little lower than that from the TPR spectrum in Fig. 3, which may be attributed to a much smaller amount of the sample (0.018 g) in the DRIFTS than that in the transient response method (2 g).

4. Acknowledgement

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