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Diffuse Reflectance Infrared Fourier Transform Spectra of Solid Silver Acetate*

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Abstract

The diffuse reflectance infrared fouries transform spectroscopy has been applied to directly follow the thermal decomposition of solid silver acetate (CH_3COOAg). It is found that a two weigt percent of the solid acetate in KBr powder gives excellent resolutions in all of the spectral region 400–4000 cm^{-1}, compared to resolution from the transmission infrared spectroscopy. The characteristic absorptions bands are almost assigned: 2900–3010 cm^{-1} for C–H stretching modes, 1340 cm^{-1} for CH_3 deformation mode, 1000–1050 cm^{-1} for CH_3-rocking deformation mode, 1575 and 1420 cm^{-1} COO-stretching modes, 620 and 645 cm^{-1} for COO-out of plane rocking deformation and bending mode respectively, and 460 cm^{-1} for in plane COO-rocking deformation mode.

The strength of each chracteristic absorption band is commonly and gradually reduced with elevating temperature of the ir cell containing the acetate in the He stream, caused by the gradual decomposition of solid silver acetate. All of the bands disappered by 300°C, indicating the complete decomposition of the acetate to silver, with no residual compounds on the surface.

1. Introduction

The infrared transmission technique has commonly been used to analyse powdered compounds or the species adsorbed on solids. The resolution of the absorption bands obtained, however, is not enough to distinguish the focused compounds, because of the light scattering of the sample. On the contrary, the infrared diffuse reflectance technique could be rather effective to analyse the samples which give higher light scattering. In addition, using this technique it is extremely easy to prepare the samples, whereas using the infrared transmission technique it is somewhat difficult to make the disk samples.

The combination of the diffuse reflectance technique with the fourier transform infrared technique is a vary powerful method for detecting a small amount of species like nanograms or a weak infrared absorption. A few applications of this hybrid procedure have recently appeared in Journals[1~4]. In this paper, the diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) has been applied to follow the dynamic behavior of the thermal decomposition of solid silver acetate, during elevated temperatures. The spectra obtained are compared with the results from the infrared transmission technique, and the characteristic absorption bands are assigned as far as possible.

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2. Experimental Procedure

Special grade silver acetate (CH_3COOAg) from Wako Pure Chemical Industries Ltd. was used as a sample with no further purification. The finely powderd sample and KBr were prepared by sieving them with four hundred mesh made of stainless steel. FT-IR Model 40X (JEOL) and Model 260-80 (Hitachi Ltd.) were used for the Drifts and the transmission infrared spectroscopy, respectively. The diffuse reflectance device was a Model IR-DRA 11 from JEOL.

The disk sample for the infrared transmission technique was prepared by using the ordinary procedure : KBr powder was mixed well with the acetate and the mixture was pressed with 7 kg/cm^2. In the case of the DRIFTS, the powdered mixture was put directly on to a sample holder. A schematic drawing of the sample holder is presented in Fig. 1. The volume of the sample is about 0.015 cc as can be seen in the figure. The gas for treating the sample passes under the holder which has four holes for the diffusion of the gas. This holder can be heated up to 300°C by two small heaters which are located in the body supporting holder, where the temperature should be raised very slowly for fear destroying the KBr window. The KBr window is very close to the sample holder so as to eliminate the gas phase absorption of ir. Thus the dead space of the reactor is as small as about 0.02 cc.

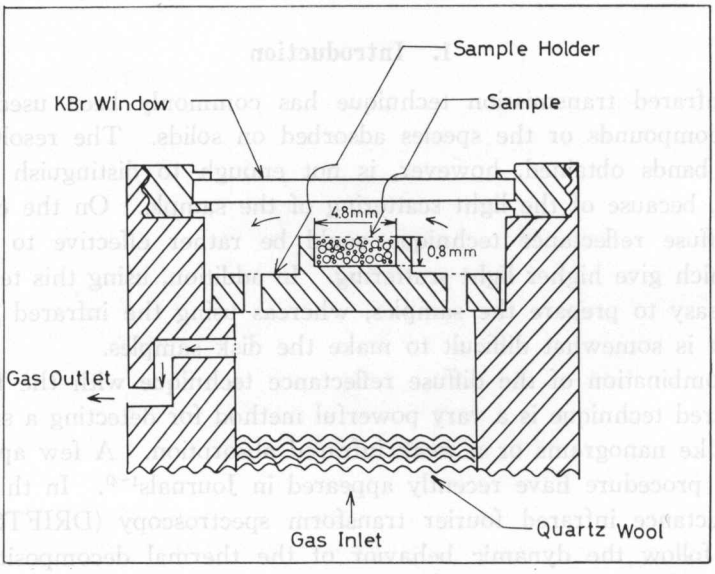

Fig. 1. Schematic drawing of IR cell for the DRIFTS.

Fig. 2 shows a schematic diagram of the hole apparatus for the DRIFTS connected to a gas flow system which is conveniently used to change gas composition in a stepwise fashion[5,6]. The flow controlling system can prepare any gas mixture which is led to the diffuse reflectance device (11). A four way

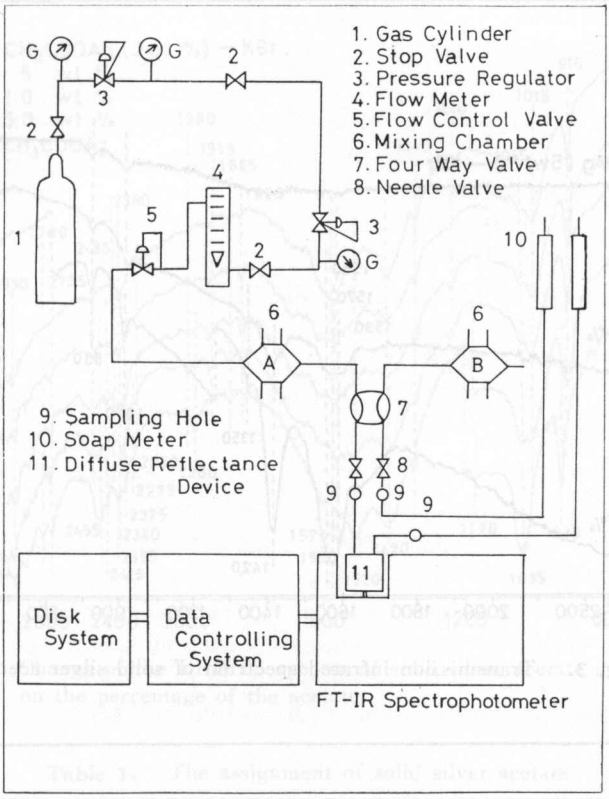

Fig. 2. Schematic diagram of the apparatus of DRIFTS with gas flow controlling system.

valve (7) is employed for the step change in gas composition, with no change in the gas flow rate from gas flow system A to B. The total gas flow rate is commonly used at 30 cc/min for all experiments.

3. Experimental Results and Discussion

3-1. Transmission Infrared Spectroscopy

Conventional transmission infrared spectroscopy did not give a good resolution for solid CH_3COOAg, as can be seen from Fig. 3. 0.5 weight percent of acetate gave the best resolution, even though there were no bands in the 2900-~3000 cm^{-1} region which was for CH-stretching modes.

3-2. Application of DRIFTS to the thermal Decomposition of Silver Acetate

It should be necessary to confirm the change of the back ground absorption of KBr depending on the elevated temperature. Fig. 4 shows the stability of the back ground of KBr when elevating the ir cell temperature from room temperature to 300°C. One can observe no appreciable change in the back ground spectrum of KBr powder. The absorption bands of around 2350 cm^{-1} correspond to gas phase carbon dioxide in air, and a large number of fine absorption in the

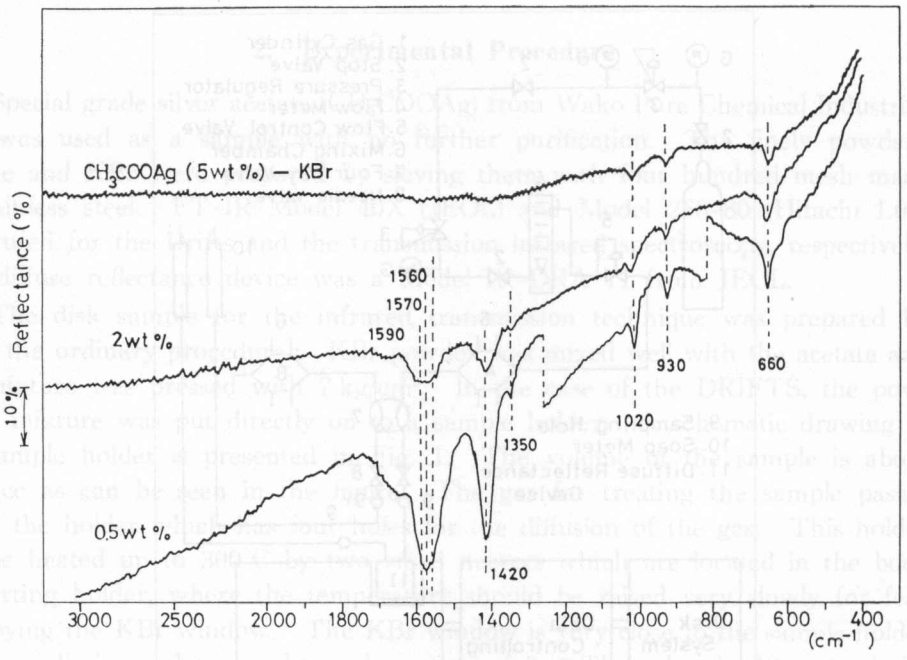

Fig. 3. Transmission infrared spectrum of solid silver acetate

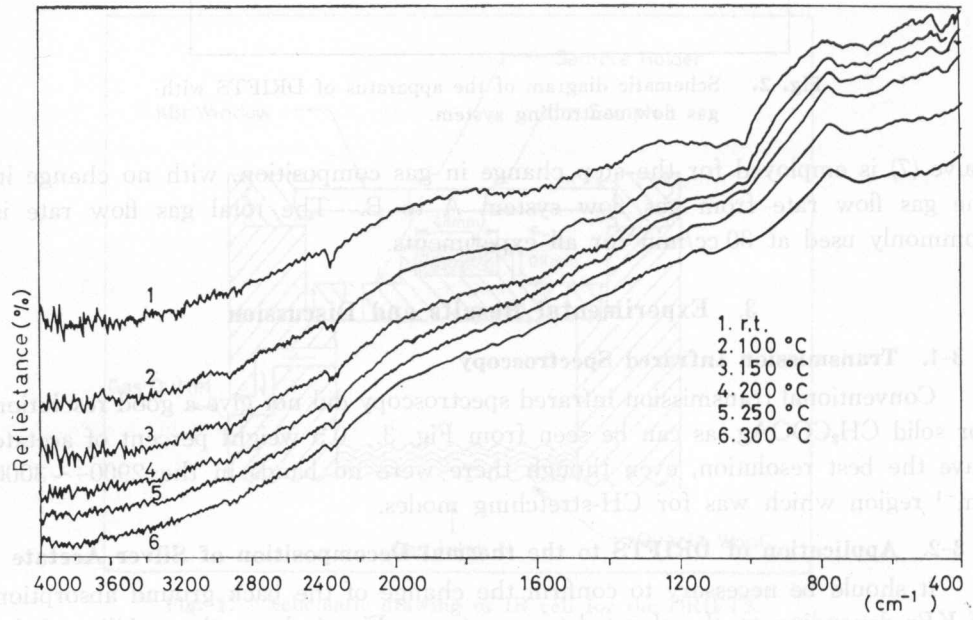

Fig. 4. The change of the back ground spectrum of DRIFTS for KBr when raising temperature.

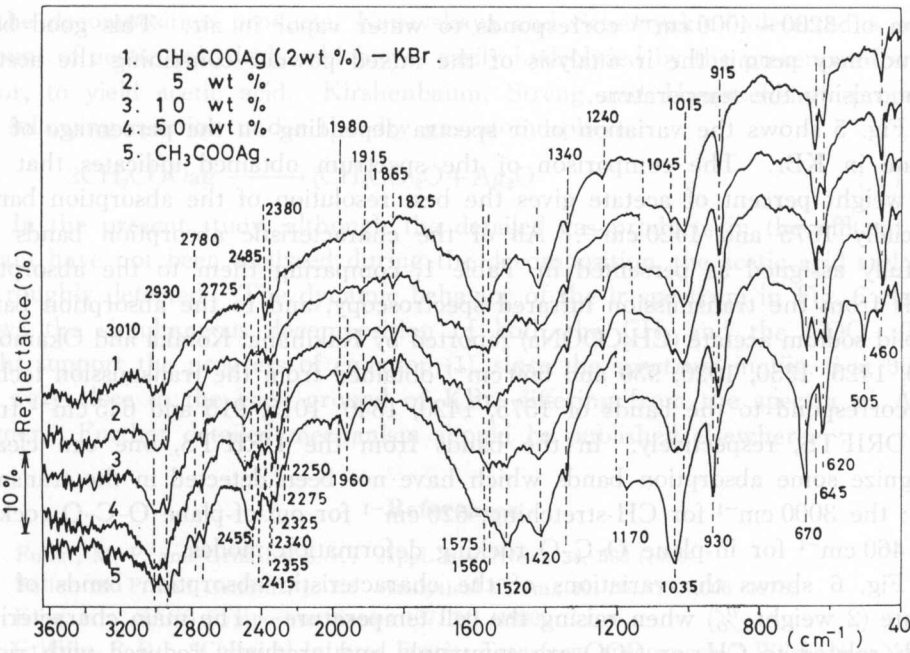

Fig. 5. Change of the DRIFTS spectra of solid silver acetate depending on the percentage of the acetate.

Table 1. The assignment of solid silver acetate

Assignment	frequency (cm^{-1})		
	CH_3COONa*	CH_3COOAg**	CH_3COOAg***
asym C–H stretch	3002	3010	—
	2974	—	—
sym C–H stretch	2930	2930	—
asym C–O stretch	1570	1575	1570
asym CH_3 deform	1447	—	—
	1407	—	—
sym C–O stretch	1423	1420	1420
	—	1240	—
sym CH_3 deform	1332	1340	1350
out of plane CH_3 rock	1045	1045	—
in plane CH_3 rock	1012	1015	1020
C–C stretch	922	915	930
O–C–O bend	650	645	660
out of plane O–C–O rock	625	620	—
in plane O–C–O rock	467	460	—

* The data by Kakihana et al. (7).
** The data by DRIFTS.
*** The data by Infrared Transmission Technique.

region of 3200～4000 cm^{-1} corresponds to water vapor in air. This good back ground may permit the ir analysis of the mixed powder containing the acetate when raising the temperature.

Fig. 5 shows the variation of ir spectra depending on the percentage of the acetate in KBr. The comparison of the spectrum obtained indicates that the two weight percent of acetate gives the best resolution of the absorption bands, especially 1575 and 1420 cm^{-1}. All of the characteristic absorption bands are carefully assigned as persented in Table 1, comparing them to the absorption bands from the transmission infrared spectroscopy, and to the absorption bands of solid sodium acetate (CH_3COONa) reported by Kakihana, Kotaka and Okamoto[7] 1570, 1420, 1350, 1020, 930 and 660 cm^{-1} obtained from the transmission technique correspond to the bands of 1575, 1420, 1340, 1015, 915 and 645 cm^{-1} from the DRIFTS, respectively. In the bands from the DRIFTS, one can clearly recognize some absorption bands which have not been detected in the transmission : the 3000 cm^{-1} for CH-stretching, 620 cm^{-1} for out-of-plane O-C-O rocking and 460 cm^{-1} for in-plane O-C-O rocking deformation modes.

Fig. 6 shows the variations of the characteristic absorption bands of the acetate (2 weight %) when raising the cell temperature. The main characteristic bands related to CH_3 or COO are commonly and gradually reduced with rising temperature, indicating no residual compounds on the surface at 300°C. In earlier works,[8~11] the decomposition of solid silver acetate had been explained as follows,

$$4CH_3COOAg \longrightarrow 3CH_3COOH + CO_2 + C + 4Ag \qquad (1)$$

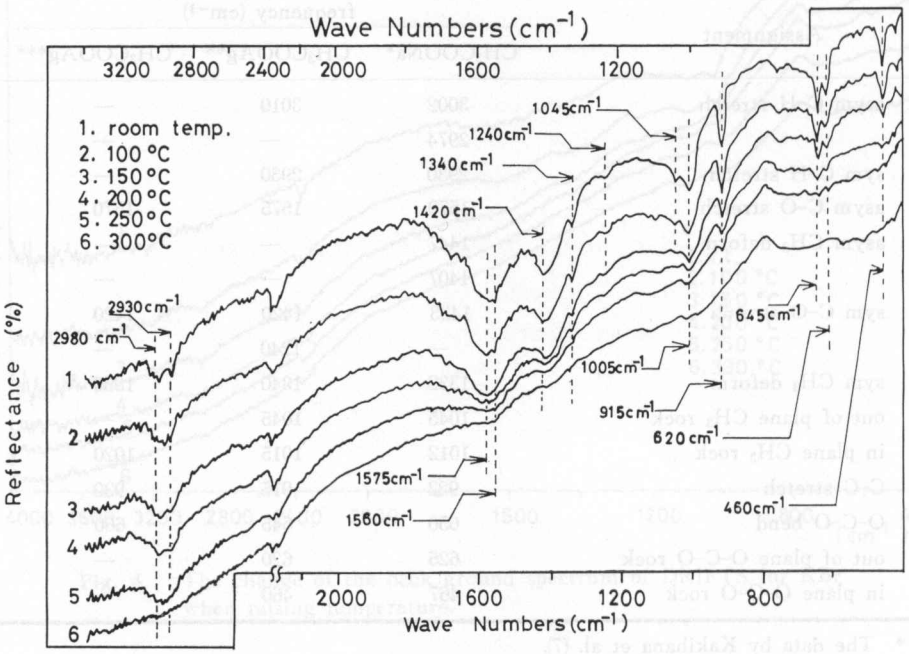

Fig. 6. Change of the DRIFTS spectra under the decomposition of solid silver acetate.

In the decomposition products, Kanevskaya and Schemyakin[13] detected a small amount of acetic anhydride which was easily hydrolyzed by the presence of water vapor, to yield acetic acid. Kirshenbaum, Streng and Hauptschein[14] proposed the following reaction under the dry gas atomosphere,

$$2CH_3COOag \longrightarrow (CH_3CO)_2O + Ag_2O \qquad (2)$$

In the present study, although the detailed gas products in the effluent gas stream have not been analysed during the decomposition, the acetic acid and CO_2 are roughly detected. The dynamic behavior of the ir spectrum in Fig. 6 clearly shows the simultaneous decomposition of both the CH_3 and the COO. This might support the progress of equation (1), since the spectrum in Fig. 6 at 300°C was very close to the back ground of KBr, differing from the spectra of Ag_2O powder. Further detailed mechanism should be published elsewhere.

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