# In Situ IR Observation of Surface Species during the Photocatalytic Decomposition of Acetic Acid over $TiO_2$ Films

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Surface-enhanced IR absorption spectroscopy (SEIRAS) was applied to in-situ observation of the adsorption states and the photocatalytic decomposition of acetic acid on $Au/TiO_2$ and $Au/Pt/TiO_2$ films. The adsorption states of acetic acid were determined in both the liquid and gas phase, and molecular adsorption was found to be dominant in the gas phase. Pt deposition on the $TiO_2$ film led to the formation of adsorbed methyl during the photodecomposition of gas-phase acetic acid, indicative of the formation of methyl radical as a reaction intermediate. The addition of gas-phase water to the system led to a significant increase in the coverage of adsorbed methyl as a result of enhancement in the reaction rate as reported before.

## 1. Introduction

In-situ observation of surface species during surface reactions such as heterogeneous catalytic processes is one of the important techniques to investigate a reaction mechanism. IR spectroscopy is probably the best method for this purpose among surface spectroscopies, because it is inexpensive, usable even at atmospheric pressure, and capable of determining chemical species.[1] The sensitivity of IR spectroscopy is, however, much lower than those of other surface vibrational spectroscopies such as HREELS, and in-situ observation during a reaction is virtually impossible in the presence of gas- or liquid-phase mediums that adsorb IR intensively.

Surface-enhanced IR absorption (SEIRA) has been observed for molecules adsorbed on an evaporated thin film of a free-electron metal such as Au or Ag and applied to surface analysis as SEIRA spectroscopy (SEIRAS).[2−12] When SEIRAS is carried out in attenuated-total-reflection (ATR) configurations, it has a great advantage that IR measurements can be carried out even in an aqueous solution, because an IR beam hardly passes through the solution.[6,9] Since the metal films used in SEIRAS are discontinuous and island-structure, SEIRAS can detect chemical species, which exist not only on the metal films but also in the vicinity of the metal islands, as evidenced previously.[11,12] In the present study we applied SEIRAS to in-situ observation of surface species formed during the photocatalytic decomposition of acetic acid over bare and platinized $TiO_2$ film surfaces, on which an Au island film was deposited.

The photocatalytic decomposition of carboxylic acids over semiconductor surfaces is called photo-Kolbe reaction,[13] and has been intensively studied as a typical photocatalytic reaction over platinized $TiO_2$ powders, which function as microphotoelectrochemical cells.[14] The photo-Kolbe reaction of liquid-phase $CH_3COOH$ was first investigated by Kreutler and Bard,[13] who found that the reaction on bare as well as on platinized $TiO_2$ powders mainly gives $CH_4$ and $CO_2$ while the photoelectrochemical (PEC) reaction of $CH_3COOH$ in a $TiO_2-Pt$ PEC cell gives $C_2H_6$ at a $TiO_2$ photoanode and $H_2$ at a Pt cathode. They explained this difference between a powdered system and a single-crystal system in terms of the following mechanism:[13]

$$h\nu \xrightarrow{TiO_2} h^+ + e^- \quad (1)$$

$$CH_3COOH \rightarrow CH_3COO^-(a) + H^+ \quad (2)$$

$$CH_3COO^-(a) + h^+ \rightarrow \cdot CH_3 + CO_2 \quad (3)$$

$$H_2O + h^+ \rightarrow \cdot OH + H^+ \quad (4)$$

$$CH_3COOH + \cdot OH \rightarrow \cdot CH_3 + CO_2 + H_2O \quad (5)$$

$$2\cdot CH_3 \rightarrow C_2H_6 \quad (6)$$

$$H^+ + e^- \xrightarrow{Pt} H(a) \quad (7)$$

$$\cdot CH_3 + H(a) \rightarrow CH_4 \quad (8)$$

$$2H(a) \xrightarrow{Pt} H_2 \quad (9)$$

For the reaction on powdered $TiO_2$, the density of $\cdot CH_3$ radicals is very low due to the large surface area of powdered $TiO_2$, and the sites for $\cdot CH_3$ production are very close to the sites for H(a) formation. As a result, the reaction of $\cdot CH_3$ radicals with H(a) (eq 8) occurs more favorably than the dimerization of $\cdot CH_3$ radicals (eq 6). For the reaction in a PEC cell, on the other hand, $TiO_2$ photoanode is a single crystal, specific surface area of which is very low, and H(a) is formed at a Pt counter electrode spatially separated from $TiO_2$ photoanode. As a result, the dimerization of $\cdot CH_3$ radicals dominates. We have also studied the photo-Kolbe reaction of gas-phase $CH_3COOH$ over $Pt/TiO_2$ powders, and found the drastic enhancement of $C_2H_6$ formation upon the addition of gas-phase $H_2O$.[15,16] This enhancement was ascribed to the acceleration of $CH_3COOH$ decomposition by $\cdot OH$ radicals formed from $H_2O$ (eq 5). The reaction on bare $TiO_2$ is very slow, giving $CH_4$ and $CO_2$, while the loading of Pt significantly promotes the reaction with a change in main products to $H_2$, $CO_2$, and $C_2H_6$.[16] Au loading

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instead of Pt loading, however, gives little effect on a reaction rate as well as on product distribution, since Au is quite inactive for hydrogen evolution.

Since radical formation was assumed for the photocatalytic reaction of $CH_3COOH$, ESR detection of radical species was attempted during the reaction, and $\cdot CH_3$ radical was detected using a spin trapping reagent.[17,18] More recently, Kaise et al.[19] employed a flow-cell ESR and directly observed $\cdot CH_3$ and $\cdot CH_2COOH$ radicals in aqueous metal/$TiO_2$ suspensions at room temperature. Nosaka et al.[20] also detected $\cdot CH_3$ radical in the flow ESR measurements and assumed two reaction path ways for $\cdot CH_3$ radical formation from its dependence on a flow rate. Thus, $\cdot CH_3$ radical formation in the photocatalytic decomposition of $CH_3COOH$ has been confirmed for aqueous Pt/$TiO_2$ suspensions.

On the basis of the results obtained so far, the effects of Pt loading and $H_2O$(g) addition on the photocatalytic decomposition of $CH_3COOH$ will be examined by SEIRAS.

## 2. Experimental Section

The details of sample preparation and experimental setup have been described in previous papers.[11,12] Briefly, a transparent $TiO_2$ film coated on a $CaF_2$ disk (30 mm in diameter, 2 mm thick) by a standard sol−gel method was used as a photocatalyst. The disk was dipped into a $TiO_2$ sol prepared by the hydrolysis of Ti isopropoxide in 2-propanol, followed by drying in a $N_2$ atmosphere for 5 h and calcination in air at 500 °C for 3 h. $TiO_2$ films prepared by repeating this procedure three times exhibited pale blue color. Although the thickness of the films was not measured, it was estimated less than 500 nm from its transparency. Au and Pt deposition on the $TiO_2$ films was made by an evaporation method under a vacuum of $3 \times 10^{-8}$ Torr. The thickness of metal films was monitored with a quartz film-thickness meter (Inficon XTM/2) and the deposition rate was controlled at 0.18 nm/min. The average thickness of the Au film was ca. 6 nm, while that of the Pt film ca. 1 nm.

For a gas-phase reaction, an evacuable IR cell was used, which was connected to a pumping and gas handling system. SEIRAS measurements were carried out in a backside reflection mode,[11,12] in which an IR beam from FTIR (Horiba FT-300) was introduced from the $CaF_2$ side of the sample at the incident angle of ca. 50° and reflected at the interface between the $TiO_2$ and Au films. The reflected IR beam was collimated to an external MCT detector at liquid nitrogen temperature. This method enables us to observe surface species without the disturbance of IR absorption by gas- or liquid-phase reactants and products such as an ATR method. SEIRA spectra were recorded with the resolution of 4 $cm^{-1}$ and with 200 scan. Acetic acid (99.5%) was used without further purification. Water and acetic acid were deaerated by repeating a freeze-and-thaw cycle for a gas-phase reaction. The vapor of water or acetic acid was introduced into the cell from a gas handling system equipped with a Baratron pressure gauge. A 1:1 mixture of gas-phase water and acetic acid was prepared by mixing their vapor at the same pressure in a glass reservoir. The light source was a high-pressure Hg lamp (Ushio UIV-570) that was filtered through a band-pass filter (Toshiba UV-D33S, 240−400 nm) and a water filter (10 cm long) to remove heat.

## 3. Results and Discussion

SEIRAS measurements were first applied to the adsorption of $CH_3COOH$ in an aqueous solution, and the SEIRA spectra of $CH_3COOH$ adsorbed on the Au/$TiO_2$ film were successfully recorded as shown in Figure 1. In this measurement, liquid water

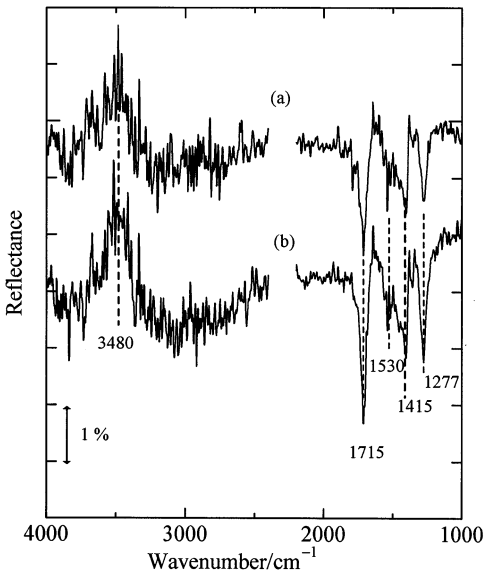


**Figure 1.** SEIRA spectra of $CH_3COOH$ adsorbed on Au/$TiO_2$ in an aqueous $CH_3COOH$ solution. The spectrum of adsorbed water was subtracted. $CH_3COOH$ concentration, (a) 8.3 vol %; (b) 16.6 vol %.

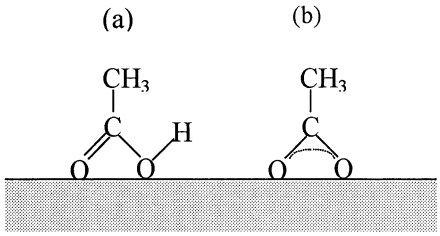


**Figure 2.** Adsorption states of (a) $CH_3COOH$ and (b) $CH_3COO^-$ on the sample.

was added first to the cell, followed by recording SEIRA spectrum as background, and then a calculated amount of $CH_3COOH$(l) was added to the cell. Therefore, the spectrum of adsorbed water is subtracted in Figure 1. The concentration of $CH_3COOH$ is 8.3 vol % for spectrum (a) and 16.6 vol % for (b). An intense band at 1715 $cm^{-1}$ is assigned to the C═O stretching of carboxyl, while bands at 1530 and 1415 $cm^{-1}$ are attributable to the antisymmetric and the symmetric stretching of O−C−O, respectively.[21] The band at 1277 $cm^{-1}$ is assigned to the stretching of C−O. A broad negative band around 3480 $cm^{-1}$ is due to a decrease in the O−H stretching band of adsorbed water, i.e., the removal of adsorbed water from the surface by $CH_3COOH$ adsorption. The O−H stretching of $CH_3COOH$ is very broad and weak in its aqueous solution, since it is partly ionized. No bands due to C−H stretching were observed. This is probably because the detection range of SEIRAS is so short (∼1 nm) from a probe metal[1,10] that the methyl groups of adsorbed $CH_3COOH$ would not be detected when $CH_3COOH$ adsorbs on the surface by COOH.

Since $CH_3COOH$ exhibits the stretching bands of C═O, C−O, and O−H, while $CH_3COO^-$ exhibits the antisymmetric and the symmetric stretching bands of O−C−O, these results indicate that both of them are adsorbed on the surface. Because SEIRAS is sensitive only to vibrational modes perpendicular to the surface (surface selection rule),[1] adsorbed $CH_3COOH$ and $CH_3COO^-$ would be oriented perpendicular to the surface as shown in Figure 2. One may suspect that the spectra observed here are the transmission spectra of $CH_3COOH$ and $CH_3COO^-$, which enter into the bulk of $TiO_2$ film, since the film made by a sol−gel method is porous. If this were the case, then the Au

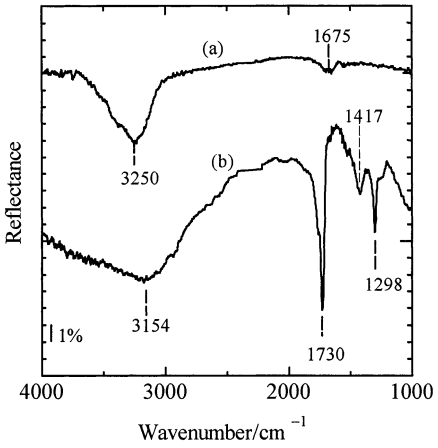


**Figure 3.** SEIRA spectra of (a) $H_2O$ and (b) $CH_3COOH$ adsorbed from gas phase onto $Au/TiO_2$. $H_2O$ pressure, 10 Torr; $CH_3COOH$ pressure, 15 Torr.

film functions as a simple mirror. Au films are not necessarily SEIRA active, for example, when prepared under low vacuum conditions or deposited at a higher rate. The lack of SEIRA enhancement may be due to contaminations of the surface or the formation of continuous metal film. Such SEIRA inactive Au films give no spectrum in the presence of adsorbed species, even though it works as a mirror. This rules out the possibility that the SEIRA spectrum involves the transmission spectrum of species in the pores of the $TiO_2$ film. The $TiO_2$ films used are so thin that adsorbed species on the films could not be detected in an IR transmission mode.

Although $TiO_2$ films coated on a $CaF_2$ disk were stable in an aqueous $CH_3COOH$ solution in the dark, the films were found to undergo dissolution to some extent under band gap illumination. Since SEIRAS is able to detect an atomic level change in surface composition, the photodissolution of $TiO_2$ films is a fatal problem. Since the films were found stable under illumination in the presence of gas-phase $CH_3COOH$, the gas-phase photoreaction was investigated by SEIRAS to obtain reproducible results. Figure 3a shows the SEIRA spectrum of $H_2O$ adsorbed at 10 Torr of $H_2O$(g), while Figure 3b shows the spectrum of $CH_3COOH$ adsorbed from $CH_3COOH$(g) at 15 Torr. The spectral intensities of surface species adsorbed from gas phase were as good as those from liquid phase. All the spectra disappeared upon evacuating the cell, indicative of the physisorption of adsorbed species. The spectrum of $CH_3COOH$ is very similar to those observed for $CH_3COOH$(l), but some differences are noticeable. The 1417 $cm^{-1}$ band assigned to the symmetric stretching of O−C−O is much lower in intensity than the 1730 $cm^{-1}$ band assigned to the C═O stretching, indicating that $CH_3COO^-$(a) is smaller in amount than $CH_3COOH$(a) as compared to the liquid-phase case. This may be due to the absence of $H_2O$(l), which could promote the ionization of $CH_3COOH$. The broad band centered at 3154 $cm^{-1}$ is the OH stretching of $CH_3COOH$.

The $Au/TiO_2$ sample was exposed to a 1:1 mixture of $CH_3COOH$(g) and $H_2O$(g) at 15 Torr, and then irradiated to investigate a photoreaction mechanism. Difference SEIRA spectra between before and after UV irradiation are shown in Figure 4. The bands at 1734, 1410, and 1294 $cm^{-1}$ decrease in intensity, and new bands appear at 3250 and 1592 $cm^{-1}$. Negative bands at 1734, 1294, and 1410 $cm^{-1}$ indicate a decrease in the amounts of $CH_3COOH$(a) and $CH_3COO^-$(a). A weak band at 1592 $cm^{-1}$ is attributed to surface carbonate species, which may be produced by the reaction of $CH_3COO^-$ or $CO_2$, which is a product of the reaction, with $TiO_2$ surface.

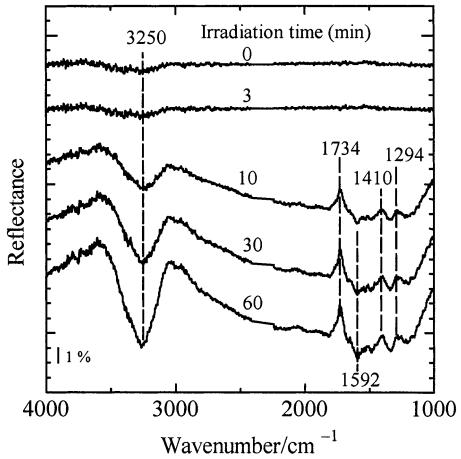


**Figure 4.** Difference spectra between before and after irradiation to $Au/TiO_2$ in the presence of a 1:1 mixture of $CH_3COOH$(g) and $H_2O$(g) at 15 Torr.

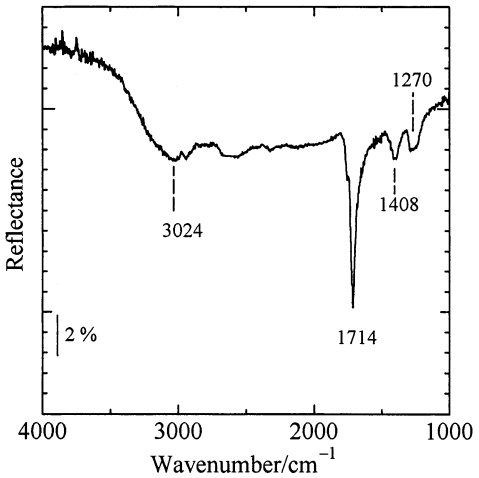


**Figure 5.** SEIRA spectrum of $CH_3COOH$ adsorbed on $Au/Pt/TiO_2$ from $CH_3COOH$(g) at 15 Torr.

The decrease of $CH_3COOH$(a) and $CH_3COO^-$(a) may be due to the increase of reaction intermediates such as carbonates and photoadsorbed water, which compete for adsorption sites. An increased band at 3250 $cm^{-1}$ is assigned to the O−H stretching of adsorbed $H_2O$, which is produced by the oxidation of $CH_3COOH$. The photoenhanced adsorption of $H_2O$ could occur as reported previously.[12] No other species were formed on the $Au/TiO_2$ film surfaces during the reaction.

To examine the effects of Pt loading on a reaction mechanism, the photodecomposition of $CH_3COOH$(g) over $Au/Pt/TiO_2$ film was investigated by SEIRAS. Figure 5 shows SEIRA spectrum of $CH_3COOH$ adsorbed on $Au/Pt/TiO_2$ film from neat $CH_3COOH$(g) at 15 Torr, which is basically identical with that observed for the $Au/TiO_2$. Therefore, Pt loading gives no effects on the adsorption states of $CH_3COOH$. Figure 6 shows difference spectra before and after UV irradiation in the presence of neat $CH_3COOH$(g) at 15 Torr. Negative bands at 1714, 1412, and 1296 $cm^{-1}$ indicate the decrease of $CH_3COOH$(a) and $CH_3COO^-$(a) as already observed for the reaction on $Au/TiO_2$. A broad band at 3274 $cm^{-1}$ is assigned to the stretching of surface OH. The reason for this OH formation in the absence of $H_2O$(g) will be discussed later. Two weak bands at 2985 and 2878 $cm^{-1}$ are assigned to the C−H asymmetric and symmetric stretching of adsorbed $CH_3$, respectively. The formation of $CH_3$(a) is a crucial difference between the reactions on $Au/TiO_2$ and on $Au/Pt/TiO_2$, and would afford a clue to a

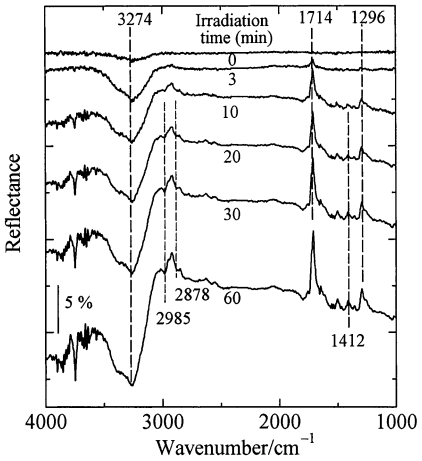


**Figure 6.** Difference spectra between before and after irradiation to $Au/Pt/TiO_2$ in the presence of neat $CH_3COOH(g)$ at 15 Torr.

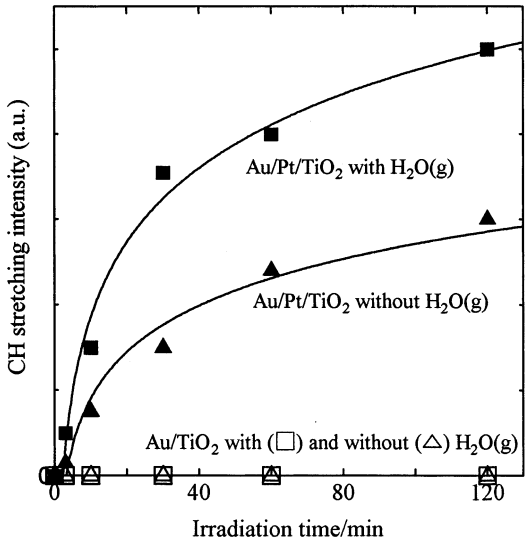


**Figure 7.** Time dependence of the band intensities of C−H stretching during the photocatalytic decomposition of $CH_3COOH(g)$ on $Au/TiO_2$ and $Au/Pt/TiO_2$ in the presence and absence of $H_2O(g)$.

mechanism of the reaction. A sharp band at 3750 $cm^{-1}$ was not reproducible and would be due to a systematic error of the spectroscopy, since a dynamic range of our FTIR machine is too narrow to accumulate accurately low-intensity signals in this region. We have found that the addition of $H_2O(g)$ drastically enhances the photocatalytic reaction of $CH_3COOH(g)$ on $Pt/TiO_2$.[15,16] To examine the effects of $H_2O(g)$, SEIRAS measurements were carried out for the photocatalytic reaction of a 1:1 mixture $CH_3COOH(g)$ and $H_2O(g)$. Spectral features were virtually identical with those observed for the reaction of neat $CH_3COOH(g)$, but the bands attributed to $CH_3(a)$ grew up at a higher rate than in the absence of $H_2O(g)$ as shown in Figure 7. This result would be resulted from acceleration of the reaction by the addition of $H_2O(g)$ as reported before.

The present SEIRAS measurements show that $CH_3(a)$ is formed during the photodecomposition of $CH_3COOH(g)$ on $Au/Pt/TiO_2$ but not on $Au/TiO_2$. The formation of $CH_3(a)$ could arise from the adsorption of $\cdot CH_3$ radicals on the surface, and the coverage of $CH_3(a)$ may depend on the rate of $\cdot CH_3$ radical formation. For the reaction of $CH_3COOH(g)$, $\cdot CH_3$ radicals would not be stabilized by hydration unlike in aqueous solutions so that they would be spontaneously adsorbed on the surface. The photodecomposition of $CH_3COOH$ on bare $TiO_2$ is known to be much slower than that on $Pt/TiO_2$.[13,16] The absence of $CH_3(a)$ in the reaction on $Au/TiO_2$ is basically due to the slow decomposition of $CH_3COOH$. On the other hand, the addition of $H_2O(g)$ enhances the photodecomposition of $CH_3COOH(g)$ on $Pt/TiO_2$ as mentioned above, and as a result, the coverage of $CH_3(a)$ increases, as shown in Figure 7, due to an increase in the concentration of $\cdot CH_3$ radicals. One may suppose here that the reaction of $\cdot CH_3$ radicals with H(a) (eq 8) would be also enhanced by the addition of $H_2O(g)$, since H(a) production is also enhanced. The formation of $CH_4$ is, however, less enhanced by the addition of $H_2O(g)$ to the photodecomposition of $CH_3COOH(g)$ over $Pt/TiO_2$ than the formation of $C_2H_6$.[15,16] This arises from its reaction mechanism, in which H(a) is produced on Pt sites, while $\cdot CH_3$ radical formation occurs on $TiO_2$ sites.[13,14] Therefore, $CH_4$ formation requires the migration of $\cdot CH_3$ radicals from $TiO_2$ sites to Pt sites or the spillover of H(a) from Pt sites to $TiO_2$ sites.

A question in the present SEIRAS measurements is a significant increase in O−H stretching band during the photodecomposition of neat $CH_3COOH(g)$ on $Au/Pt/TiO_2$ (Figure 6). One of the reasons for this O−H band increase is transformation of $H_2O(a)$, which remains after room-temperature pumping, toward a strongly adsorbed one under irradiation as reported previously.[12] This transformation is accompanied by OH band shift to lower frequencies.[12] Another factor is the adsorption of impurity $H_2O$ (0.5%) in acetic acid. These factors are, however, too small to explain the large increase of OH band, since the amount of $H_2O(a)$ remained after pumping as well as impurity $H_2O$ in $CH_3COOH$ is very small. There should be, therefore, other factors to increase the O−H band. Although all H(a) atoms are thought to desorb as $H_2$ in eq 9, some H(a) atoms may spill over from Pt to $TiO_2$ surfaces and hydrogenate $TiO_2$ to produce surface hydroxyls. In addition a $TiO_2$ film prepared by a sol−gel method undergoes photodissolution under acidic conditions, which may also produce surface hydroxyls.

In summary, in-situ SEIRAS can determine the adsorption states of $CH_3COOH$ on $TiO_2$ films and detect reaction intermediates such as $CH_3(a)$ during the photocatalytic decomposition of $CH_3COOH$. These observations could not be performed by conventional IR spectroscopy. Thus, SEIRAS is a promising spectroscopy to observe submonolayer quantities of surface species in the presence of reactants and to investigate a mechanism of catalytic processes.

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