

## 1P181

SFG 分光法による Pt(111) 基板上的 TiO<sub>2</sub> 膜に吸着したホルメートの観察  
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### [Introduction]

Titanium oxide is widely applied as catalyst support, photocatalyst, gas sensors, coatings, and *etc.* These applications are essentially associated with its surface properties, therefore, which have received considerable studies by FT-IR, TPD, electron spectroscopies and STM techniques in recent years. In present study, titanium oxide film was prepared on Pt(111) in the ultra high vacuum (UHV) chamber. Formic acid is used as a molecular probe to characterize the surface sites on the titanium oxide film. At the same time, sum frequency generation (SFG) spectroscopy, which is a highly surface-specific technique, is applied to investigate the configurations of surface species. It is observed that bidentate or bridge formate is formed by the decomposition of formic acid on the titanium oxide film. Furthermore, we are going to apply the time-resolved SFG technique to this system.

### [Experimental]

The SFG setup and the UHV instruments are the same as previous reports [1]. A clean Pt(111) surface was obtained by repeated Ar ion bombardment and annealing at 1000 K until the cleanliness and orderliness were confirmed by AES and LEED observations. The titanium oxide film (10-20 Å thickness) was deposited on Pt(111) at 700 K by vacuum evaporation of Ti while  $1 \times 10^{-6}$  Torr O<sub>2</sub> flow was presented [2]. After cooled to 250 K, the titanium oxide film was exposed to 1000 L (1 L =  $1 \times 10^{-6}$  Torr s) of DCOOD. For the SFG measurement, frequency-tunable IR and 532 nm visible pulse (pulse width of 35 ps) were used. Those energies at sample surface were 50 μJ/pulse (at 2000 cm<sup>-1</sup>) and 100 μJ/pulse, respectively. For the TPD record, a 2.8 K/s heating rate was used, and six mass numbers were monitored simultaneously.

### [Results and discussion]

The temperature programmed desorption (TPD) spectra for saturation exposure of formic acid on titanium oxide film at 250 K is shown in figure 1. One desorption region clearly appear on the spectra between 340 and 450 K. CO<sub>2</sub> is main product, which desorption peak locates at 390 K. On the other hand, no DCOOD signal was detected. This indicates that these desorption products are not from QMS cracking of formic acid but from the decomposition of surface species formed after exposure of formic acid on the titanium oxide film. Compared with our previous TPD results of formic acid on NiO(111) surface [3], the mass spectrum signals are much weak even that of CO<sub>2</sub> in this case. This suggests that the amount of the species produced on the surface of the titanium oxide is small.

Figure 2 shows the SFG spectrum for saturation exposure of formic acid on the titanium oxide film at 250 K, and the thermal stability of surface species was investigated. Both visible pulse and IR pulse were *p*-polarization. At 250 K, it exhibits only one

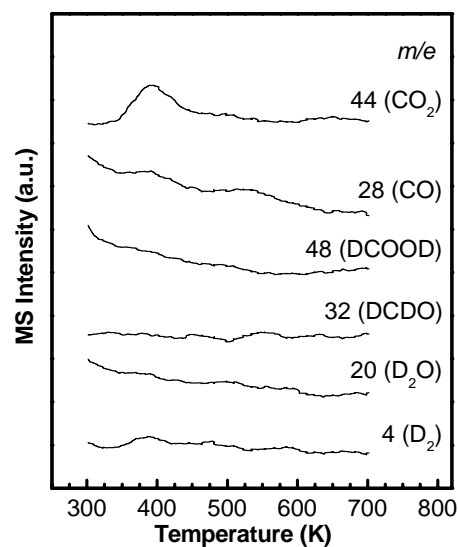


Fig. 1. TPD spectra for saturation exposure of DCOOD on titanium oxide film at 250 K

vibrational resonance band at  $2170\text{ cm}^{-1}$ , which is assigned to the  $\nu(\text{C-D})$  vibrational mode of bidentate or bridge formate, demonstrating that formate is produced by the dissociation of formic acid on the surface of the titanium oxide film. After the formate was formed on the titanium oxide film at 250 K, the substrate was heated step by step. It is observed that the above band is reduced at 400 K and disappears on further heating to 450 K. Compared with the TPD results, this illustrates that formate adsorbed on the titanium oxide film decomposes at around 400 K and the main product is  $\text{CO}_2$ . Exposure dependent SFG spectra were also carried out. It gives that the vibrational band at  $2170\text{ cm}^{-1}$  achieves strongest intensity around 1000 L. This indicates that the adsorption of formate on titanium oxide is very slow and the apparent sticking probability was approximately 0.001.

On the other hand, as shown in figure 2, there is no vibrational signal of monodentate formate, which frequency locates at around  $2200\text{ cm}^{-1}$ . Considering the band at  $2170\text{ cm}^{-1}$  is broad, we also carried out the SFG measurement with different polarization combinations. Shown in figure 3, after the change in polarization of the visible pulse from *p*-polarization to *s*-polarization, the SFG signal at  $2170\text{ cm}^{-1}$  disappears. This means that the C-D bond, corresponding to this vibrational band, is vertical to the surface of titanium oxide film, further confirming this band at  $2170\text{ cm}^{-1}$  belongs to the bidentate or bridge formate because the C-D bond of monodentate is tilted from the surface normal. This behavior of formate adsorbed on the titanium oxide is different from that on  $\text{NiO}(111)$ , on which surface both types of formate are formed by the decomposition of formic acid. This suggests that the distance between two coordinatively unsaturated surface Ti cations, which act as lewis acid sites bonded with formate, is suitable to the formation of bridge formate.

In summary, formate by the dissociation of formic acid on the titanium oxide film is sensitively detected by SFG spectroscopy. From the orientation of C-D bond, it indicates that formate exists as bidentate or bridge structure.

### [References]

1. J. Kubota, E. Yoda, N. Ishizawa, A. Wada, K. Domen, S. S. Kano: *J. Phys. Chem. B* **107**, 10329 (2003)
2. A. B. Boffa, H. C. Galloway, P. W. Jacobs, J. J. Benitez, J. D. Batteas, M. Salmeron, A. T. Bell, G. A. Somorjai: *Surf. Sci.* **326**, 80 (1995)
3. A. Bandara, J. Kubota, A. Wada, K. Domen, C. Hirose: *Surf. Sci.* **364**, L580 (1996)

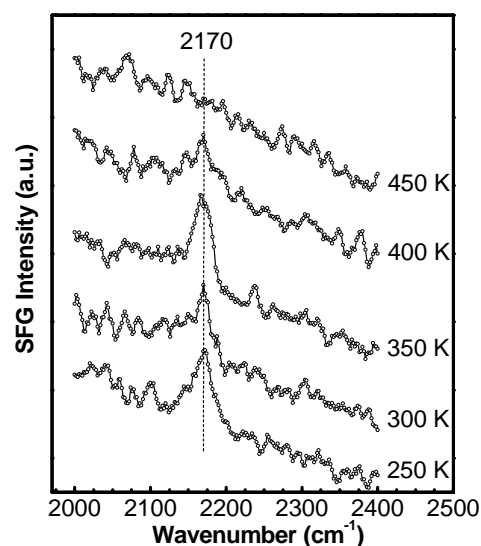


Fig. 2. SFG spectra for saturation exposure of DCOOD on titanium oxide film at different temperatures

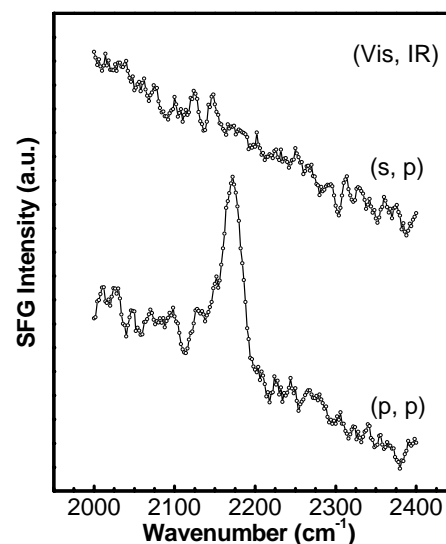


Fig. 3. SFG spectra of formate adsorbed on titanium oxide film at 250 K for different polarization combinations