Time-Resolved Sum Frequency Generation Reveals Adsorbate Migration between Different Surface Active Sites on Titanium Oxide/Pt(111)

Jun Chen, Jun Kubota, Akihide Wada, Junko Nomura Kondo, and Kazunari Domen*

Japan Science and Technology Agency, 4-1-8 Hon-cho, Kawaguchi-shi, Saitama 332-0012, Japan, Department of Chemical System Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan, and Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuda, Midori-ku, Yokohama 226-8503, Japan

Received January 5, 2009; E-mail: domen@chemsys.t.u-tokyo.ac.jp

Titanium oxide is used extensively as photocatalysts, catalyst supports, coatings, and in solar cell materials.[1] As the utility of titanium oxide in such applications is essentially attributable to the unique surface properties of this compound, its surface structure and adsorption and reaction properties have received considerable attention.[2-7] Surface-scanning probe analyses have revealed that the surface of titanium oxide consists of various-fold-coordinated Ti and O atoms and includes defects such as oxygen vacancies.[3,8] Moreover, the different surface sites of titanium oxide have different activities for catalytic reactions.[6,9,10] However, due to the limits of temporal resolution and sensitivity for many of the analytical techniques, few studies have provided insights into the kinetic processes of adsorbates on the titanium oxide surface. Such information, however, is crucial to clarify the catalytic reaction mechanism for this oxide. Recently, adsorbate hopping on $TiO_2(110)$ was suggested on the basis of static scanning tunneling microscopy (STM) observations.[5] In the present study, we adopt time-resolved sum frequency generation (SFG) spectroscopy in combination with a laser-induced temperature jump technique, in real time, to resolve the transient motion of formate on the surface of titanium oxide film supported on Pt(111).

Titanium oxide films were prepared on Pt(111) substrates by the same method as employed in a previous study.[10] Briefly, the titanium oxide film was deposited at 700 K in an O_2 atmosphere and then annealed at 873 K under vacuum for several minutes. Similar to the observations by Boffa et al.,[11] the sample annealed for 6.0 min (TiO_x/Pt(111)-873-6) exhibits low energy electron diffraction (LEED) spots (see Figure S1). The structure of the TiO_x film develops rectangular symmetry upon annealing, resulting in a surface similar to that of reduced $TiO_2(110)$ as supported by STM observations. After cooling to 200 K, samples were exposed to 1000 Langmuir (1 Langmuir = 1×10^{-6} Torr s) of deuterated formic acid (DCOOD), which decomposed into formate and deuterium atoms on the surface of the TiO_x film.[2,5,10] The formate species generated thus reflects the state of the surface active sites.

The vibrational structure of adsorbates on solid surfaces can be analyzed by infrared−visible SFG spectroscopy, which is highly surface-specific due to a nonlinear optical process.[12] In our work, the time-resolved SFG signal is obtained using the combination of frequency-tunable infrared and 532-nm visible probe pulses (35 ps pulse width) on the sample surface, where irradiation of 1064-nm pump pulses (2 mJ/pulse, 35 ps pulse width, 4 mm spot diameter) induces a temperature jump. Based on the extent of the vibrational frequency shift for the surface OD group and the calculation of heat diffusion,[13] the surface temperature jump is estimated to be ca. 60 K for an ultrathin titanium oxide film (5−7 Å in thickness) supported on Pt(111). The surface temperature change returns to the half-maximum in ~100 ps.
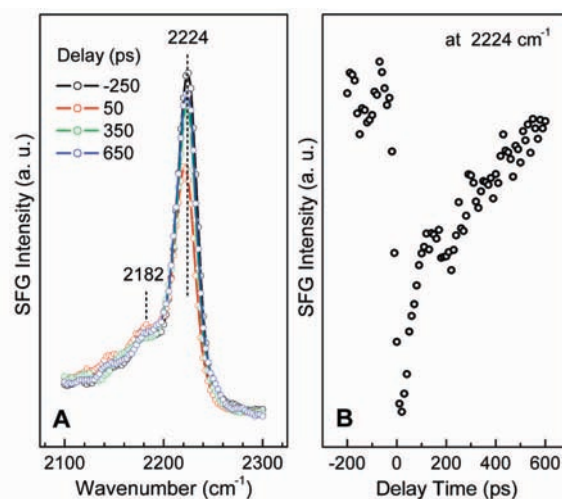
Figure 1. Time-resolved SFG analysis of formate adsorbed on TiO_x/Pt(111)-873-6 at 200 K. (A) SFG spectra of formate before (−250 ps, black line) and after (50 ps, red; 350 ps, green; 650 ps, blue) excitation of the surface with a 1064-nm pump pulse. (B) Temporal change in SFG intensity of formate vibration at 2224 cm^{-1} with respect to the pump pulse.

Figure 1A shows the transient SFG spectra of formate adsorbed on TiO_x/Pt(111)-873-6 before and after a temperature jump. This sample produces two vibrational bands: a prominent band at 2224 cm^{-1} and a much weak band at 2182 cm^{-1}. As discussed previously,[10] the high-frequency band is assignable to the $\nu(C-D)$ vibrational mode of formate bound to ordered Ti^{4+} sites by bridging coordination, and the low-frequency band is attributable to the $\nu(C-D)$ vibrational mode of formate associated with surface defect sites consisting of Ti^{3+} (e.g., oxygen vacancies). Upon the surface temperature jump, the band at 2224 cm^{-1} is weakened markedly but recovers after ~650 ps. As shown in Figure 1B, the signal at 2224 cm^{-1} is weakened immediately upon irradiation and then recovers to the half-maximum in ~100 ps, consistent with the surface temperature profile. Similar spectral behavior was also observed in the present study for CO adsorbed on Pt(111) and formate adsorbed on the as-prepared TiO_x/Pt(111) (see Figures S2 and S3).

In general, two effects can be considered as causes for this spectral behavior: (i) the excitation of low-frequency frustrated modes of formate by laser-induced heating, which affects the $\nu(C-D)$ vibration through anharmonic coupling,[14] and (ii) a change in the population of the formate due to desorption, transportation over different surface sites, or hopping between different configurations. For TiO_x/Pt(111)-873-6, the latter effect can be excluded because the signal recovered after 650 ps, no new $\nu(C-D)$ band was detected, and the change in the band at 2182 cm^{-1} was found to be negligible.
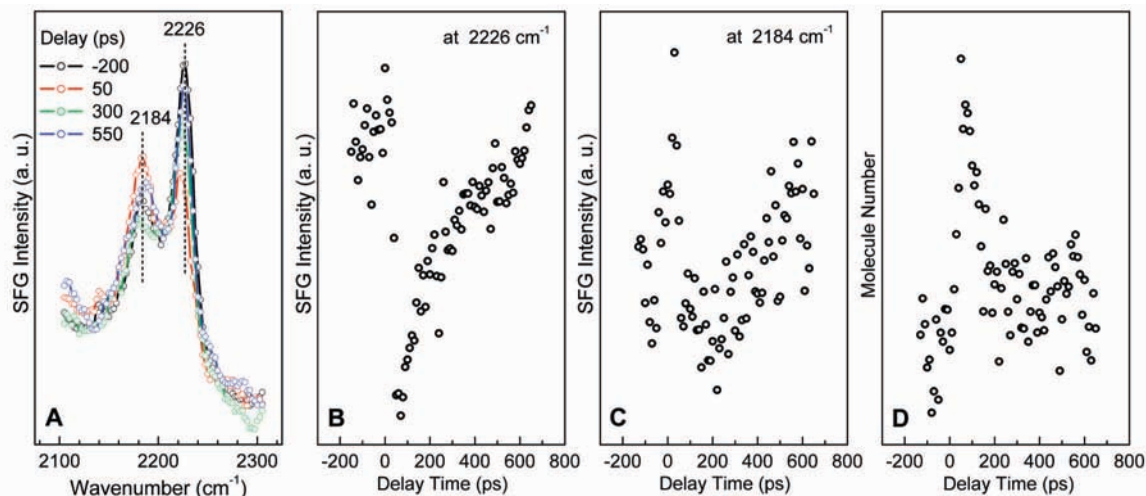
Figure 2. Time-resolved SFG analysis of formate adsorbed on TiO$_x$/Pt(111)-873-4 at 200 K. (A) SFG spectra of formate before (−200 ps, black line) and after (50 ps, red; 300 ps, green; 550 ps, blue) excitation of the surface with a 1064-nm pump pulse. (B,C) Temporal change in SFG intensities at 2226 and 2184 cm^{-1}, corresponding to formate adsorbed on ordered Ti^{4+} sites and defect sites, respectively. (D) Temporal change in calculated population of formate adsorbed on defect sites.

The sample annealed for 4.0 min (TiO$_x$/Pt(111)-873-4) was found to have a relatively high density of surface defect sites.[10] Figure 2 shows the SFG results for formate adsorbed on TiO$_x$/Pt(111)-873-4. As expected, this defect-rich sample displays a moderate vibrational band at 2184 cm^{-1} as well as a stronger band at 2226 cm^{-1}. Upon the surface temperature jump, the intensity of the high-frequency band decreases abruptly but eventually recovers after ∼650 ps. Interestingly, the low-frequency band is affected in a different manner. Upon the surface temperature jump, the signal intensity initially increases (50 ps), then decreases (300 ps), and finally increases (550 ps) again to values higher than that prior to excitation.

The temporal change in these signal intensities are shown in Figure 2B and 2C. The change of the low-frequency band is considered to be due to both the anharmonic coupling with frustrated modes and the change in formate population, as described in (i) and (ii) above. The initial strengthening of the low-frequency signal indicates that the population of formate adsorbed on defect sites increases upon heating. That is, heating drives transportation of formate from ordered Ti^{4+} sites (2226 cm^{-1} band) to defect sites (2184 cm^{-1} band), since desorption is negligible in the experimental conditions. The square relationship between SFG intensity and molecule number allows the change in the population of formate adsorbed on defect sites to be determined, as shown in Figure 2D (see Supporting Information for derivation and theoretical explanation). Distinct time-dependent motion of formate between ordered Ti^{4+} sites and defect sites can thus be resolved. This behavior was also observed in the present study for TiO$_x$/Pt(111) annealed for 4.5 min (see Figure S4). It is estimated based on these calculations that the number density of formate adsorbed on defect sites increases by ca. 20% upon the surface temperature jump. The enthalpy difference (ΔH) between these two formate species is estimated to be ca. 3 kJ mol^{-1}, based on the van't Hoff equation.[13]

The previous static investigations show that, for TiO$_x$/Pt(111)-873-6, the thermal decomposition of formate adsorbed on ordered Ti^{4+} sites occurs at temperatures above 320 K; however, for TiO$_x$/Pt(111)-873-4, it occurs at much lower temperatures and in phase with the thermal decomposition of formate adsorbed on defect sites.[10] These different reaction behaviors can be explained by the present observation of formate migration on these two different surface active sites.

In conclusion, time-resolved SFG spectroscopy in combination with a laser-induced temperature jump has revealed the heat-driven migration of formate between different surface active sites on titanium oxide film.

Supporting Information Available: Materials and methods; Transient SFG spectra for CO adsorbed on Pt(111), formate adsorbed on the as-prepared TiO$_x$/Pt(111) and on TiO$_x$/Pt(111)-873-4.5; Derivation and theoretical explanation of transient signal change. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Hashimoto, K.; Irie, H.; Fujishima, A. *Jpn. J. Appl. Phys., Part 1* **2005**, *44*, 8269–8285. (b) Zhao, W.; Ma, W. H.; Chen, C. C.; Zhao, J. C.; Shuai, Z. G. *J. Am. Chem. Soc.* **2004**, *126*, 4782–4783. (c) Routray, K.; Reddy, K.; Deo, G. *Appl. Catal. A: Gen.* **2004**, *265*, 103–113. (d) Mor, G. K.; Varghese, O. K.; Paulose, M.; Shankar, K.; Grimes, C. A. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 2011–2075.
(2) Onishi, H.; Aruga, T.; Iwasawa, Y. *J. Catal.* **1994**, *146*, 557–567.
(3) Diebold, U. *Surf. Sci. Rep.* **2003**, *48*, 53–229.
(4) Sedona, F.; Rizzi, G. A.; Agnoli, S.; Xamena, F.; Papageorgiou, A.; Ostermann, D.; Sambi, M.; Finetti, P.; Schierbaum, K.; Granozzi, G. *J. Phys. Chem. B* **2005**, *109*, 24411–24426.
(5) Aizawa, M.; Morikawa, Y.; Namai, Y.; Morikawa, H.; Iwasawa, Y. *J. Phys. Chem. B* **2005**, *109*, 18831–18838.
(6) Bikondoa, O.; Pang, C. L.; Ithnin, R.; Muryn, C. A.; Onishi, H.; Thornton, G. *Nat. Mater.* **2006**, *5*, 189–192.
(7) (a) Zhang, J.; Xu, Q.; Feng, Z.; Li, M.; Li, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 1766–1769. (b) Li, S. C.; Zhang, Z.; Sheppard, D.; Kay, B. D.; White, J. M.; Du, Y.; Lyubinetsky, I.; Henkelman, G.; Dohnalek, Z. *J. Am. Chem. Soc.* **2008**, *130*, 9080–9088.
(8) (a) Fukui, K.; Onishi, H.; Iwasawa, Y. *Phys. Rev. Lett.* **1997**, *79*, 4202–4205. (b) Rohrer, G. S.; Henrich, V. E.; Bonnell, D. A. *Science* **1990**, *250*, 1239–1241.
(9) (a) Li, G.; Dimitrijevic, N. M.; Chen, L.; Nichols, J. M.; Rajh, T.; Gray, K. A. *J. Am. Chem. Soc.* **2008**, *130*, 5402+. (b) Henderson, M. A. *J. Phys. Chem. B* **1997**, *101*, 221–229.
(10) Chen, J.; Kubota, J.; Wada, A.; Kondo, J. N.; Domen, K. *J. Phys. Chem. C* **2008**, *112*, 12477–12485.
(11) Boffa, A. B.; Galloway, H. C.; Jacobs, P. W.; Benitez, J. J.; Batteas, J. D.; Salmeron, M.; Bell, A. T.; Somorjai, G. A. *Surf. Sci.* **1995**, *326*, 80–92.
(12) (a) Zhu, X. D.; Suhr, H.; Shen, Y. R. *Phys. Rev. B* **1987**, *35*, 3047–3050. (b) Hirose, C.; Akamatsu, N.; Domen, K. *J. Chem. Phys.* **1992**, *96*, 997–1004.
(13) (a) Hirose, C.; Bandara, A.; Katano, S.; Kubota, J.; Wada, A.; Domen, K. *Appl. Phys. B: Laser Opt.* **1999**, *68*, 559–565. (b) Kubota, J.; Wada, A.; Domen, K.; Kano, S. S. *Chem. Phys. Lett.* **2002**, *362*, 476–482.
(14) Backus, E. H. G.; Eichler, A.; Kleyn, A. W.; Bonn, M. *Science* **2005**, *310*, 1790–1793.

JA900052W