THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

pubs.acs.org/JPCL

Photoinduced Decomposition of Formaldehyde on a TiO_2(110) Surface, Assisted by Bridge-Bonded Oxygen Atoms

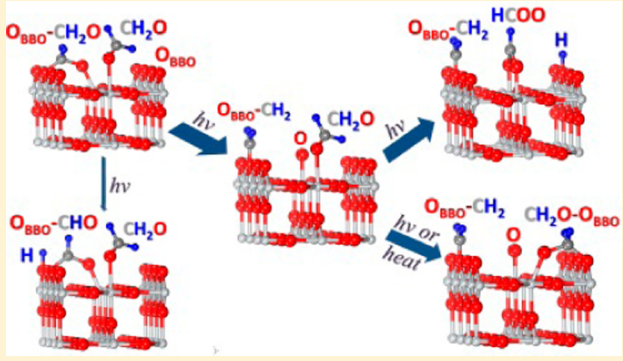
Chenbiao Xu,[†,§] Wenshao Yang,[†] Qing Guo,*[,†] Dongxu Dai,[†] Timothy K. Minton,*[,†,‡] and Xueming Yang*[,†]

[†]State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, 457 Zhongshan Road, Dalian 116023, Liaoning, P. R. China

[‡]Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717, United States

Supporting Information

ABSTRACT: We have investigated the photoinduced decomposition of formaldehyde (CH_2O) on TiO_2(110) at 400 nm using temperature-programmed desorption. Formate (HCOO), methyl radicals (CH_3), and ethylene (C_2H_4) have been detected, while no evidence of polymerization of CH_2O was found. The initial step in the decomposition of CH_2O on TiO_2(110) is the formation of a dioxymethylene intermediate in which the carbonyl O atom of CH_2O is bound both to a Ti atom on the five-fold-coordinated lattice site (Ti_{5C}) and to a nearby bridge-bonded oxygen (BBO) atom. During 400 nm irradiation, the dioxymethylene intermediate can transfer methylene to the bridging oxygen row and break the C−O bond, thus leaving the original carbonyl O atom on the Ti_{5C} site. After this transfer of methylene, several pathways to products are available. Thus we have found that BBO atoms are intimately involved in the photoinduced decomposition of CH_2O on TiO_2(110).



SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

TiO_2 has been investigated as a potential energy-efficient catalyst for photo-oxidation.[1−8] The development of efficient catalysts from TiO_2 can be facilitated by an understanding of the site-specific surface dynamical processes of adsorbed molecules and reaction intermediates. Much work has been done to study the photocatalysis of organic compounds on TiO_2, for example, the degradation of CH_2O[9] and the development of a TiO_2-based gas sensor.[10] However, most of the studies are on powders of TiO_2.[11−13] To clarify the role of different kinds of active sites and gain a better understanding of photocatalytic reactions, single crystals[14−20] and thin films[12,13] of TiO_2 have been used as model surfaces for studying photo-oxidation and other photoinduced processes. Among the rutile TiO_2 surfaces, the (110) single-crystal surface has been especially widely used in fundamental studies of photocatalytic reactions as well as for studies of adsorbate−surface interactions, surface reconstructions, defects, and many other phenomena.

It has been demonstrated that surface Ti^{3+} defect sites,[21−24] bulk Ti^{3+} defect sites,[25] and surface Ti^{4+} sites[26,27] on TiO_2(110) play important roles in molecular adsorption, thermal reactions, and photocatalytic reactions. There are also some suggestions in the literature that lattice oxygen plays a role in photo-oxidation reactions on TiO_2 mainly because of its presence in products or intermediates (as determined through isotopic labeling studies).[28−32] However, a direct mechanistic experimental study of how lattice oxygen is involved in photochemical reactions on TiO_2 has not been reported. In this work, we have conducted a temperature-programmed desorption (TPD) investigation of the mechanism of the photoinduced decomposition of CH_2O on a TiO_2(110) surface and have identified the important role of the bridge-bonded oxygen (BBO) atoms in the first step toward the final reaction products: formate, C_2H_4, and CH_3.

Figure 1 shows TPD spectra collected at mass-to-charge ratios (m/z) of 28 (CO^+, $C_2H_4^+$) and 29 (HCO^+) after surfaces of TiO_2(110) were dosed with 0.55 ML of CH_2O and then irradiated by a laser at 400 nm for various durations. Before irradiation, the signal profile of the 280 K peak from m/z = 28 and 29 was exactly the same as that from m/z = 30 (CH_2O^+; see in Figure S1 in Supporting Information), suggesting that all of these peaks are the result of dissociative ionization of the desorbed parent CH_2O molecule in the electron-bombardment ionizer. An additional, weak peak with the same shape was collected at m/z = 31, which is presumably the result of the ions, $CHDO^+$ and $HC^{18}O^+$, that originate from naturally abundant isotopologues of formaldehyde. The respective

Received: June 30, 2013
Accepted: July 26, 2013
Published: July 26, 2013

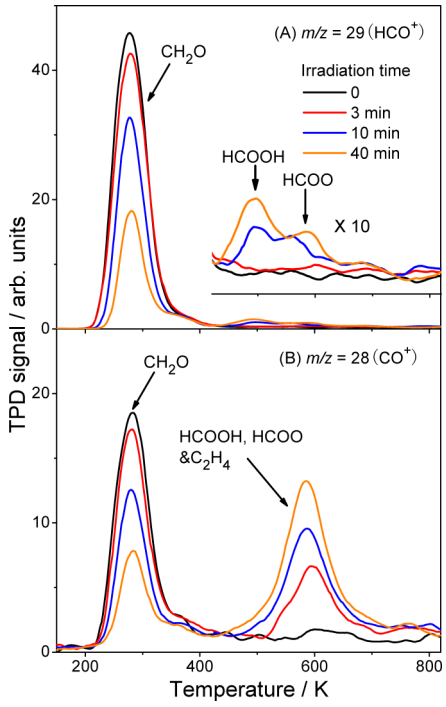


Figure 1. Reduced $TiO_2(110)$ was dosed with 0.55 ML of CH_2O at 110 K. (A) Typical TPD spectra collected at m/z = 29 (HCO^+) following different laser irradiation times. (B) Typical TPD spectra collected at m/z = 28 ($C_2H_4^+$, CO^+) following different laser irradiation times.

relative intensities at m/z = 29, 30, and 31 may be compared with tabulated intensities of these ion fragments for the formaldehyde monomer (1, 0.58, and 0.005) and the cyclic formaldehyde trimer, 1,3,5-trioxane (0.26, 0.15, and 1).[33] The observed fragmentation intensity ratios clearly indicate that the desorption is strongly dominated by formaldehyde monomers. The CH_2O peak at 280 K decreases monotonically as the laser irradiation time increases, suggesting that the CH_2O molecules that are adsorbed on the Ti_{5C} sites of $TiO_2(110)$ either desorb or react to form other products.

A 360 K shoulder becomes obvious in the m/z = 29 TPD spectrum after irradiation (Figure 1A), suggesting the formation of a product that is more strongly bound to the surface than CH_2O. Taking into account additional TPD traces (Figure S1, Supporting Information), the 360 K shoulder is also assigned to CH_2O. Recent theoretical results[34,35] show that a dioxymethylene structure involving CH_2O can form on a $TiO_2(110)$ surface, where the carbonyl O atom of CH_2O is bound both to a Ti_{5C} site and to an adjacent BBO atom. This structure has an adsorption energy of 1.1 to 1.3 eV, which implies that it is more stable than molecularly adsorbed CH_2O that is bound to the surface solely through an $O-Ti_{5C}$ bond (0.5 to 0.6 eV). Previous Fourier-transform infrared (FTIR) spectroscopy results of CH_2O adsorption on fully oxidized (defect-free) and reduced (with O-atom vacancies) TiO_2 surfaces are suggestive of two adsorption modes in which one is an η^1 configuration (O adsorption structure) and the other an η^2 configuration (C, O adsorption structure).[36−38] High-resolution electron energy loss spectroscopy (HREELS) studies[39] of CH_2O on $TiO_2(110)$ clearly observed a C−O stretching vibration in O−C−O units, and the authors attributed this observation to paraformaldehyde formation on the $TiO_2(110)$ surface. However, later TPD investigations[40,41] of formaldehyde polymerization on $TiO_2(110)$ and on a $(WO_3)_3/TiO_2(110)$ model catalyst found no evidence of paraformaldehyde formation, as the sole desorption of CH_2O monomers was clearly evident on $TiO_2(110)$. This conclusion is similar to that from a previous formaldehyde polymerization study with powders of TiO_2 and $(WO_3)_3/TiO_2$.[42] Therefore, we conclude that a dioxymethylene structure involving adsorbed CH_2O on $TiO_2(110)$ is the only candidate for the HREELS observation of a C−O stretching vibration in O−C−O units and our observation of the increasing 360 K shoulder after irradiation.

Two additional new desorption features at 486 and 580 K grow in the m/z = 29 TPD spectrum with increasing irradiation times. TPD traces were collected at a variety of m/z ratios to assign the new features (Figure S1 in Supporting Information). Compared with previous studies of HCOOH adsorbed on $TiO_2(110)$[43] and the cracking pattern of HCOOH observed in our mass spectrometer (see Figure S2 in Supporting Information), the 486 K peak here is assigned to the recombination of surface formates with surface hydroxyl groups at BBO sites, and the 580 K peak at m/z = 29 is assigned to the desorption of formates and, possibly, of a secondary CH_2O product from the decomposition of formates.

Concomitant to the decrease in the CH_2O TPD peak, the TPD signal for m/z = 28 at 580 K increases with increasing laser irradiation times (Figure 1B). The m/z = 28 signal at 580 K may come from three sources. The first is an ethylene (C_2H_4) product that arises from CH_2O adsorbed on oxygen defect sites to form a diolate ($-OCH_2CH_2O-$) species, which releases C_2H_4 at a relatively high TPD temperature near 620 K.[21,39] Taking into account correction factors for mass spectrometer sensitivity and assuming all of the signal in the m/z = 28 TPD peak comes from C_2H_4 before irradiation, the ratio of C_2H_4-to-CH_2O product desorption is found to be 4%, which is consistent with an oxygen defect concentration of ~4%, as indicated by the TPD of water.[44] As indicated in Figure 1B, the other two sources of m/z = 28 signal at 580 K are HCOOH and formate, both of which could be photo-oxidation products. In previous investigations of HCOOH adsorbed on $TiO_2(110)$,[40,45−47] the main species on the surface is formate when the surface temperature is higher than 500 K. Therefore, CO is observed to desorb at 580 K as a result of the decomposition of the formate species.

The large TPD signal for desorbed CO seen in Figure 1B indicates that formate is an important photoinduced product. Compared with other products, the 580 K peak intensity is >10 times greater (see Figure S1 in Supporting Information), strongly suggesting that formate is the main product of the photoinduced decomposition of CH_2O on $TiO_2(110)$. The yields of CO (from formate) and CH_2O with irradiation time are shown in Figure 2. About 0.35 ML of CH_2O was depleted during 40 min of irradiation, whereas only 0.08 ML of formate was produced, implying that the decrease in the CH_2O signal is mainly the result of desorption of CH_2O during laser irradiation. Indeed, a large photoinduced desorption signal of CH_2O at m/z = 30 was observed during irradiation by a time-of-flight (TOF) method (see Figure S3 in Supporting Information), implying that a significant fraction of CH_2O is desorbed during irradiation.

To produce formate, the carbon atom of the reagent CH_2O molecule must acquire a second O atom. Previous studies of acetone and acetaldehyde photochemistry on preoxidized $TiO_2(110)$[18,19,48−51] demonstrate that acetone or acetaldehyde

dx.doi.org/10.1021/jz401349q | J. Phys. Chem. Lett. 2013, 4, 2668−2673

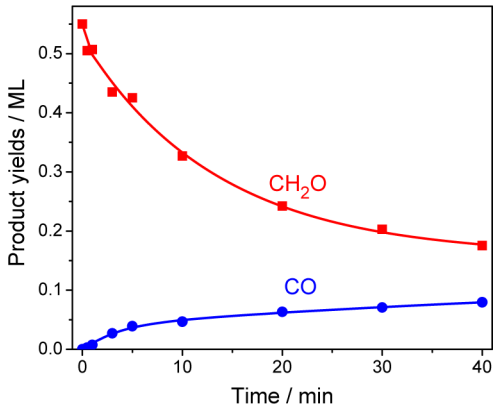


Figure 2. Yields of CH_2O and CO (from formate) as a function of irradiation time following adsorption of 0.55 ML of CH_2O on a $TiO_2(110)$ surface at 110 K, derived from data in Figure 1. The contribution of C_2H_4 has been subtracted.

adsorbed on preoxidized $TiO_2(110)$ undergoes a facile thermal reaction to form a photoactive acetone−oxygen or acetaldehyde−oxygen complex first; then, UV irradiation of the acetone−oxygen or acetaldehyde−oxygen complex results in the ejection of a methyl radical into gas phase and conversion of the surface-bound fragment into acetate or formate. Formate was also observed as the main product in our experiments, even without preoxidation of the surface, implying that CH_2O acquires an additional O atom either from a BBO row or from another CH_2O molecule adsorbed on the surface. A series of studies[40−42] show that polymerization of formaldehyde cannot be achieved by heat on pure TiO_2. In our experiments, the lack of TPD signals at $m/z > 30$ show that paraformaldehyde is not produced during UV irradiation (not shown), implying that HCOOH formation from direct reaction of two CH_2O molecules is also unlikely. The direct photodissociation of CH_2O to produce an O atom via C═O bond breakage is also not possible because of the low adsorption cross section of CH_2O at 400 nm ($\sim 10^{-23}$ cm^2).[52] Therefore, the most likely reaction must involve the transfer of methylene from CH_2O to a BBO atom during UV irradiation through an intermediate adsorption structure consisting of dioxymethylene, with the O atom of CH_2O remaining on a Ti_{5C} site. The O atom may react with a nearby adsorbed CH_2O molecule to form a CH_2O−O complex; then, formate can be produced by the transfer of an H atom to a BBO site or the ejection of the H atom into the vacuum. As shown in Figure 1A, the increasing signal intensity for recombinative desorption of HCOOH from H atoms on BBO rows and formates strongly suggests that H atoms are transferred to BBO sites from the CH_2O−O complex during UV irradiation. In addition, the increasing signal intensity for the recombinative desorption of H_2O from hydroxyls on BBO rows (see Figure S4 in Supporting Information) also verifies this reaction channel. The high background at $m/z = 1$ in the mass spectrometer made it impossible to observe an H-atom TOF signal and verify the possibility of H-atom ejection into the vacuum.

The conclusion of a dioxymethylene intermediate is supported by the observation of other products. Typical TPD spectra for $m/z = 26$ ($C_2H_2^+$) are shown in Figure 3A. As reported in previous studies,[21,39] the 620 K peak at $m/z = 26$ comes from C_2H_4, which is produced by the carbon−carbon bond formation reaction of two CH_2O molecules adsorbed on vacancy sites. A TPD spectrum at $m/z = 27$ verifies that the $m/z = 26$ signal is from the fragmentation of C_2H_4. (See Figure S1 in the Supporting Information.) The increase in the C_2H_4 signal with irradiation time is strong evidence that methylene groups are transferred to BBO atoms as a result of UV irradiation.

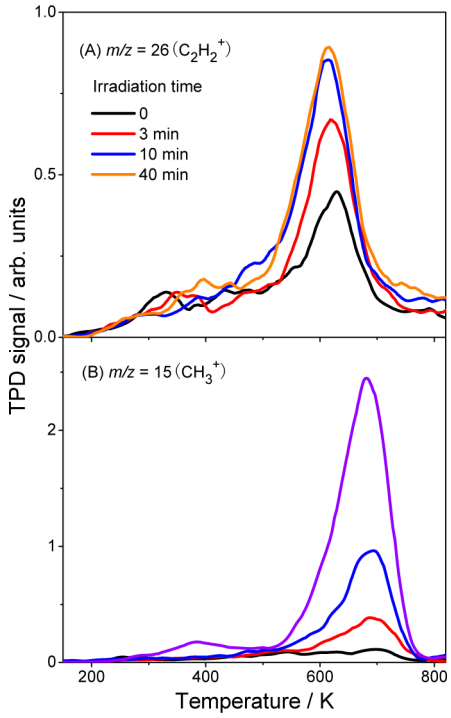


Figure 3. Reduced $TiO_2(110)$ was dosed with 0.55 ML of CH_2O at 110 K. (A) Typical TPD spectra collected at $m/z = 26$ ($C_2H_2^+$) following different laser irradiation times. (B) Typical TPD spectra collected at $m/z = 15$ (CH_3^+) following different laser irradiation times.

Another broad peak appears at 680 K in the TPD spectrum at $m/z = 15$ (CH_3^+) after irradiation and increases with irradiation time. This peak is attributed to CH_3 desorption from BBO atoms, consistent with our previous studies.[27] A separate experiment with CH_3OH-covered $TiO_2(110)$ was carried out to confirm methyl radical desorption. (See Figure S5 in Supporting Information.) However, the desorption temperature of CH_3 on BBO sites is 30 K higher than that observed in previous studies,[27] which may be due to a temperature measurement offset. The appearance and increase of CH_3 products on BBO atoms after UV irradiation further demonstrates that methylene groups can be transferred to bridging oxygen during irradiation. These methylene groups may form CH_3 by reacting with H atoms on BBO sites. The CH_3 products would adsorb on BBO sites more strongly than methylene. The yields of CH_3 and C_2H_4 following 0.55 ML adsorption of CH_2O on $TiO_2(110)$ are shown in Figure 4. The yield of C_2H_4 increases very fast to reach a plateau, while the yield of CH_3 continues to increase. After 40 min of irradiation, the total amount of methylene that has transferred to bridging oxygen is ~0.06 ML, ~0.02 ML less than the amount of formate that has been formed.

A schematic model for the photoinduced decomposition of CH_2O is depicted in Figure 5. First, two adsorption structures of CH_2O (CH_2O molecularly adsorbed to a surface Ti_{5C} atom solely through an O−Ti_{5C} bond and CH_2O molecularly adsorbed to the rutile (110) surface through O−Ti_{5C} and C−

dx.doi.org/10.1021/jz401349q | J. Phys. Chem. Lett. 2013, 4, 2668−2673

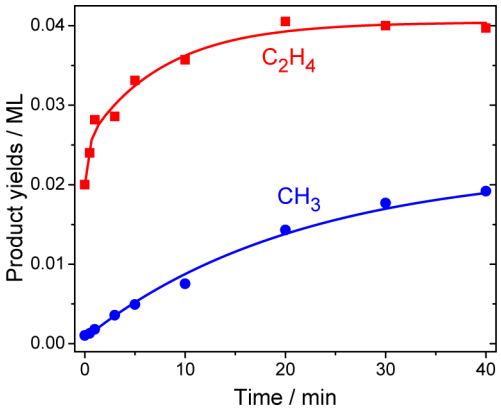


Figure 4. Yields of C_2H_2 and CH_3 as a function of irradiation time following adsorption of 0.55 ML of CH_2O on a TiO_2(110) surface at 110 K, derived from data in Figure 3.

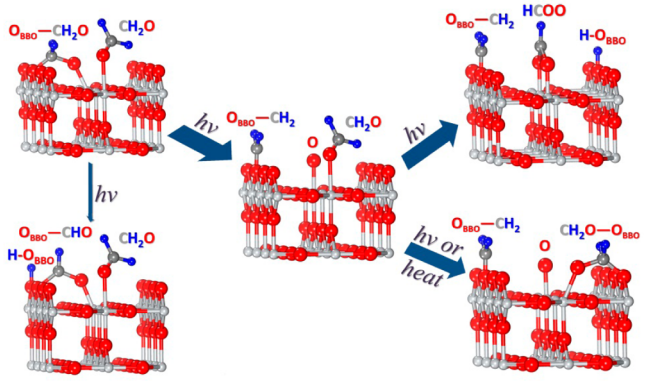


Figure 5. Schematic model for bridging-oxygen-assisted, photoinduced decomposition of CH_2O on reduced TiO_2(110).

O_{2C} (two-fold coordinated bridging oxygen) bonds) exist after exposure of 0.55 ML CH_2O to the TiO_2(110) surface. Then, the methylene of CH_2O may transfer from the dioxymethylene structure to a BBO atom through a photoinduced process, with the O atom of CH_2O remaining on a Ti_{5C} site. This O atom may react with a nearby CH_2O to form a CH_2O−O complex by heat or photon irradiation. Eventually, formate is produced when an H atom transfers to a BBO site from the CH_2O−O complex. This is the main reaction channel for formate production. The formation of the C_2H_4 and CH_3 products occurs through reactions of the methylene on the BBO rows. As previously mentioned, the amount of formate is larger than the amount of methylene that transferred to BBO sites, which suggests that another form of formate may exist. Previous STM studies of HCOOH on a TiO_2(110) surface[46,47] do show two kinds of formates. One type of formate adsorbs on the TiO_2(110) surface through two O−Ti_{5C} bonds, and the other type adsorbs through C−O−Ti_{5C} and C−O_{2C} bonds with the original C−O bond of carbonyl along the [1$\bar{1}$0] orientation on the rutile (110) surface. In the case of CH_2O adsorption, this adsorption structure is formed by transferring an H atom from dioxymethylene to a BBO site.

Our TPD investigation demonstrates that BBO atoms play a very important role in the photoinduced decomposition of CH_2O on TiO_2(110) through an initial dioxymethylene intermediate structure. Formate (of two types) is the most important product, but C_2H_4 and CH_3 are also significant. Clear mechanisms have been delineated for the participation of lattice (BBO) atoms in four decomposition pathways, including their presence in one type of formate product.

EXPERIMENTAL METHODS

TPD experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 6×10^{-11} Torr. Details of the TPD apparatus have been described elsewhere.[27] A quadrupole mass spectrometer (Extrel) was used to detect desorbing products. An extremely high vacuum of 1.5×10^{-12} Torr in the electron-impact ionization region was achieved and maintained during the experiment. The rutile TiO_2(110) crystal, obtained from Princeton Scientific and having dimensions of $10 \times 10 \times 1.0$ mm^3, was mounted on a Ta metal plate attached to a liquid-nitrogen-cooled sample holder for cooling to ∼100 K and resistive heating to >900 K. The surface was cleaned by cycles of Ar^+ sputtering and UHV annealing until common impurities on TiO_2, such as Ca, K, and C, were not detected by Auger electron spectroscopy (AES), and a sharp (1 × 1) low-energy electron diffusion (LEED) pattern was observed. After this preparation procedure, the crystal color became blue and an oxygen vacancy population of 4% remained, as gauged by water TPD.[44] Daily cleaning was accomplished by annealing the crystal at 850 K for 30 min in UHV. At room temperature, the vapor pressure of CH_2O produced from paraformaldehyde (95% purity, Sigma-Aldrich) was high enough for our experiments. The surface was dosed with 0.55 ML (1 ML = 5.2×10^{14} molecules cm^{-2}) coverage of CH_2O using a home-built, calibrated molecular beam doser at 110 K. The surface temperature typically rose to ∼130 K during subsequent irradiation. The irradiating laser light had a nominal wavelength of 400 nm, a pulse width of ∼50 fs, and a bandwidth of ∼20 nm (second-harmonic of Ti/sapphire laser, Legend Elite, Coherent, 1 kHz). The average power of the light was 150 mW, corresponding to $\sim 5.4 \times 10^{17}$ photons cm^{-2} s^{-1}. A previous study in our lab implies that multiphoton effects are not important at this photon flux.[53] The laser irradiation area on the surface was the elliptical projection of a 6 mm diameter laser beam with an angle of ∼30° between the surface parallel and laser direction. The TiO_2(110) surface was annealed in vacuum at 850 K for 20 min between TPD experiments to flatten and clean the surface. TPD signals were collected after irradiation with a heating rate of 2 K/s and with the sample facing the mass spectrometer detector.

ASSOCIATED CONTENT

Supporting Information

TPD spectra acquired at a variety of different mass-to-charge ratios after a CH_2O-adsorbed TiO_2(110) surface was irradiated by UV light. TPD spectra acquired at a variety of different mass-to-charge ratios after HCOOH was adsorbed on a TiO_2(110) surface. Time-of-flight signal of CH_2O ejected during UV irradiation. TPD spectra of H_2O after a CH_2O-adsorbed TiO_2(110) surface was irradiated by UV light. TPD spectra of CH_3 after a CH_3OH-adsorbed TiO_2(110) surface was irradiated by UV light. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: guoqing@dicp.ac.cn (G.Q.), tminton@montana.edu (T.K.M.), xmyang@dicp.ac.cn (X.Y.).

Present Address

[§]Chenbiao Xu: Also with School of Physics and Optoelectric Engineering, Dalian University of Technology, Dalian, Liaoning 116023, China.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Chinese Academy of Sciences, National Science Foundation of China, and the Chinese Ministry of Science and Technology.

■ REFERENCES

(1) Hoffmann, M. R.; Martin, S. T.; Choi, W. Y.; Bahnemann, D. W. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, *95*, 69−96.
(2) Thompson, T. L.; Yates, J. T., Jr. Surface Science Studies of the Photoactivation of TiO_2 New Photochemical Processes. *Chem. Rev.* **2006**, *106*, 4428−4453.
(3) Henderson, M. A.; Otero-Tapia, S.; Castro, M. E. The Chemistry of Methanol on the TiO_2(110) Surface: the Influence of Vacancies and Coadsorbed Species. *Faraday Discuss.* **1999**, *114*, 313−319.
(4) Gong, X.-Q.; Selloni, A.; Dulub, O.; Jacobson, P.; Diebold, U. Small Au and Pt Clusters at the Anatase TiO_2(101) Surface: Behavior at Terraces, Steps, and Surface Oxygen Vacancies. *J. Am. Chem. Soc.* **2008**, *130*, 370−381.
(5) Henderson, M. A. A Surface Science Perspective on TiO_2 Photocatalysis. *Surf. Sci. Rep.* **2011**, *66*, 185−297.
(6) Pang, C. L.; Lindsay, R.; Thornton, G. Chemical Reactions on Rutile TiO_2(110). *Chem. Soc. Rev.* **2008**, *37*, 2328−2353.
(7) Fujishima, A.; Zhang, X.; Tryk, D. TiO_2 Photocatalysis and Related Surface Phenomena. *Surf. Sci. Rep* **2008**, *63*, 515−582.
(8) Diebold, U. The Surface Science of Titanium Dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53−229.
(9) Zang, L.; Lange, C.; Abraham, I.; Storck, S.; Maier, W. F.; Kisch, H. Amorphous Microporous Titania Modified with Platinum(IV) Chloride-A New Type of Hybrid Photocatalyst for Visible Light Detoxification. *J. Phys. Chem. B* **1998**, *102*, 10765−10771.
(10) Yanga, L.; Liu, Z.; Shia, J.; Zhanga, Y.; Hua, H.; Shangguan, W. Degradation of Indoor Gaseous Formaldehyde by Hybrid VUV and TiO_2/UV Processes. *Sep. Purif. Technol.* **2007**, *54*, 204−211.
(11) Yang, Y. Z.; Chang, C.-H.; Idriss, H. Photo-Catalytic Production of Hydrogen form Ethanol over M/TiO_2 Catalysts (M = Pd, Pt or Rh). *Appl. Catal., B* **2006**, *67*, 217−222.
(12) Chang, Z.; Thornton, G. Reactivity of Thin-Film TiO_2(110). *Surf. Sci.* **2000**, *462*, 68−76.
(13) Herman, G. S.; Gao, Y.; Tran, T. T.; Osterwalder, J. X-ray Photoelectron Diffraction Study of an Anatase Thin Film: TiO_2(001). *Surf. Sci.* **2000**, *447*, 201−211.
(14) White, J. M.; Henderson, M. A. Trimethyl Acetate on TiO_2(110): Preparation and Anaerobic Photolysis. *J. Phys. Chem. B* **2005**, *109*, 12417−12430.
(15) White, J. M.; Szanyi, J.; Henderson, M. A. Thermal Chemistry of Trimethyl Acetic Acid on TiO_2(110). *J. Phys. Chem. B* **2004**, *108*, 3592−3602.
(16) Jayaweera, P. M.; Quah, E. L.; Idriss, H. Photoreaction of Ethanol on TiO_2(110) Single-Crystal Surface. *J. Phys. Chem. C* **2007**, *111*, 1764−1769.
(17) Henderson, M. A. Acetone and Water on TiO_2 (110): Competition for Sites. *Langmuir* **2005**, *21*, 3443−3450.
(18) Henderson, M. A. Relationship of O_2 Photodesorption in Photooxidation of Acetone on TiO_2. *J. Phys. Chem. C* **2008**, *112*, 11433−14440.
(19) Henderson, M. A. Photooxidation of Acetone on TiO_2(110): Conversion to Acetate via Methyl Radical Ejection. *J. Phys. Chem. B* **2005**, *109*, 12062−12070.
(20) Zehr, R. T.; Henderson, M. A. Acetaldehyde Photochemistry on TiO_2(110). *Surf. Sci.* **2008**, *602*, 2238−2249.
(21) Lu, G.; Linsebiger, A.; Yates, J. T., Jr. Ti^{3+} Defect Sites on TiO_2(110): Production and Chemical Detection of Active Sites. *J. Phys. Chem.* **1994**, *98*, 11733−11738.
(22) Farfan-Arribas, E.; Madix, R. J. Role of Defects in the Adsorption of Aliphatic Alcohols on the TiO_2(110) Surface. *J. Phys. Chem. B* **2002**, *106*, 10680−10692.
(23) Henderson, M. A.; Szanyi, J.; Peden, C. H. F. Conversion of N_2O to N_2 on TiO_2 (110). *Catal. Today* **2003**, *85*, 251−266.
(24) Lisachenko, A. A.; Mikhailov, R. V.; Basov, L. L.; Shelimov, B. N.; Che, M. Photocatalytic Reduction of NO by CO on Titanium Dioxide under Visible Light Irradiation. *J. Phys. Chem. C* **2007**, *111*, 14440−14447.
(25) Lira, E.; Wendt, S.; Huo, P.; Hansen, J. Ø.; Sreber, R.; Porsgaard, S.; Wei, Y.; Bechstein, R.; Lægsgaard, E.; Besenbacher, F. The Importance of Bulk Ti^{3+} Defects in the Oxygen Chemistry on Titania Surfaces. *J. Am. Chem. Soc.* **2011**, *133*, 6529−6532.
(26) Zhou, C.; Ren, Z.; Tan, S.; Ma, Z.; Mao, X.; Dai, D.; Fan, H.; Yang, X.; LaRue, J.; Cooper, R.; et al. Site-Specific Photocatalytic Splitting of Methanol on TiO_2(110). *Chem. Sci.* **2010**, *1*, 575−580.
(27) Guo, Q.; Xu, C.; Ren, Z.; Yang, W.; Ma, Z.; Dai, D.; Fan, H.; Minton, T. K.; Yang, X. Stepwise Photocatalytic Dissociation of Methanol and Water on TiO_2(110). *J. Am. Chem. Soc.* **2012**, *134*, 13366−13373.
(28) Zhuang, J.; Rusu, C. N.; Yates, J. T., Jr. Adsorption and Photooxidation of CH_3CN on TiO_2. *J. Phys. Chem. B* **1999**, *103*, 6957−6967.
(29) Muggli, D. S.; Falconer, J. L. Role of Lattice Oxygen in Photocatalytic Oxidation on TiO_2. *J. Catal.* **2000**, *191*, 318−325.
(30) Blount, M. C.; Buchholz, J. A.; Falconer, J. L. Photocatalytic Decomposition of Aliphatic Alcohols, Acids, and Esters. *J. Catal.* **2001**, *197*, 303−314.
(31) Lee, G. D.; Falconer, J. L. Transient Measurements of Lattice Oxygen in Photocatalytic Decomposition of Formic Acid on TiO_2. *Catal. Lett.* **2000**, *70*, 145−148.
(32) Thompson, T. L.; Panayotov, D. A.; Yates, J. T., Jr.; Martyanov, I.; Klabunde, K. Photodecomposition of Adsorbed 2-Chloroethyl Ethyl Sulfide on TiO_2: Involvement of Lattice Oxygen. *J. Phys. Chem. B* **2004**, *108*, 17857−17865.
(33) NIST Chemistry WebBook, webbook.nist.gov/chemistry.
(34) Haubrich, J.; Kaxiras, E.; Friend, C. M. The Role of Surface and Subsurface Point Defects for Chemical Model Studies on TiO_2: A First-Principles Theoretical Study of Formaldehyde Bonding on Rutile TiO_2(110). *Chem.—Eur. J.* **2011**, *17*, 4496−4506.
(35) Liu, H.; Wang, X.; Pan, C.; Liew, K. M. First-Principles Study of Formaldehyde Adsorption on TiO_2 Rutile (110) and Anatase (001) Surfaces. *J. Phys. Chem. C* **2012**, *116*, 8044−8053.
(36) Busca, G.; Lamotte, J.; Lavalley, J.-C.; Lorenzelli, V. FT-IR Study of the Adsorption and Transformation of Formaldehyde on Oxide Surfaces. *J. Am. Chem. Soc.* **1987**, *109*, 5197−5202.
(37) Kecskés, T.; Raskó, J.; Kiss, J. FTIR and Mass Spectrometric Study of HCOOH Interaction with TiO_2 Supported Rh and Au Catalysts. *Appl. Catal., A* **2004**, *268*, 9−16.
(38) Raskó, J.; Kecskés, T.; Kiss, J. Adsorption and Reaction of Formaldehyde on TiO_2-Supported Rh Catalysts Studied by FTIR and Mass Spectrometry. *J. Catal.* **2004**, *226*, 183−191.
(39) Qiu, H.; Idriss, H.; Wang, Y.; Wöll, C. Carbon−Carbon Bond Formation on Model Titanium Oxide Surfaces: Identification of Surface Reaction Intermediates by High-Resolution Electron Energy Loss Spectroscopy. *J. Phys. Chem. C* **2008**, *112*, 9828−9834.
(40) Kim, J.; Kay, B. D.; Dohnálek, Z. Formaldehyde Polymerization on $(WO_3)_3$/TiO_2(110) Model Catalyst. *J. Phys. Chem. C* **2010**, *114*, 17017−17022.
(41) Valentin, C. D.; Rosa, M.; Pacchioni, G. Radical versus Nucleophilic Mechanism of Formaldehyde Polymerization Catalyzed by $(WO_3)_3$ Clusters on Reduced or Stoichiometric TiO_2(110). *J. Am. Chem. Soc.* **2012**, *134*, 14086−14098.

(42) Chakraborty, A. K.; Chai, S. Y.; Lee, W. I. Photocatalytic Behavior of WO_3/TiO_2 in Decomposing Volatile Aldehydes. *Bull. Korean Chem. Soc.* **2008**, *29*, 494−496.
(43) Henderson, M. A. Complexity in the Decomposition of Formic Acid on the TiO2(110) Surface. *J. Phys. Chem. B* **1997**, *101*, 221−229.
(44) Zehr, R. T.; Henderson, M. A. Influence of O_2-Induced Surface Roughening on the Chemistry of Water on TiO_2(110). *Surf. Sci.* **2008**, *602*, 1507−1516.
(45) Bowker, M.; Stone, P.; Bennett, R.; Perkins, N. Formic Acid Adsorption and Decomposition on TiO_2(110) and on Pd/TiO_2(110) Model Catalysts. *Surf. Sci.* **2002**, *511*, 435−448.
(46) Sayago, D. I.; Polcik, M.; Lindsay, R.; Toomes, R. L.; Hoeft, J. T.; Kittel, M.; Woodruff, D. P. Structure Determination of Formic Acid Reaction Products on TiO_2(110). *J. Phys. Chem. B* **2004**, *108*, 14316−14323.
(47) Aizawa, M.; Morikawa, Y.; Namai, Y.; Morikawa, H.; Iwasawa, Y. Oxygen Vacancy Promoting Catalytic Dehydration of Formic Acid on TiO_2(110) by In Situ Scanning Tunneling Microscopic Observation. *J. Phys. Chem. B* **2005**, *109*, 18831−18838.
(48) Henderson, M. A. Acetone Chemistry on Oxidized and Reduced TiO_2(110). *J. Phys. Chem. B* **2004**, *108*, 18932−18941.
(49) Henderson, M. A. Effect of Coadsorbed Water on the Photodecomposition of Acetone on TiO_2(110). *J. Catal.* **2008**, *256*, 287−292.
(50) Zehr, R. T.; Henderson, M. A. Thermal Chemistry and Photochemistry of Hexafluoroacetone on Rutile TiO_2(110). *Phys. Chem. Chem. Phys.* **2010**, *12*, 8084−8091.
(51) Wilson, D. P.; Sporleder, D.; White, M. G. Final State Distributions of Methyl Photoproducts from the Photooxidation of Acetone on TiO_2(110). *J. Phys. Chem. C* **2012**, *116*, 16541−16552.
(52) Bogumil, K.; Orphal, J.; Homann, T.; Voigt, S.; Spietz, P.; Fleischmann, O. C.; Vogel, A.; Hartmann, M.; Bovensmann, H.; Frerick, J.; et al. Measurements of Molecular Absorption Spectra with the SCIAMACHY pre-Flight Model: Instrument Characterization and Reference Data for Atmospheric Remote Sensing in the 230−2380 nm Region. *J. Photochem. Photobiol. A.: Photochem.* **2003**, *157*, 167−184.
(53) Guo, Q.; Xu, C.; Ren, Z.; Yang, W.; Ma, Z.; Dai, D.; Minton, T. K.; Yang, X. Methyl Formate Production on TiO_2(110), Initiated by Methanol Photocatalysis at 400 nm. *J. Phys. Chem. C* **2013**, *117*, 5293−5300.