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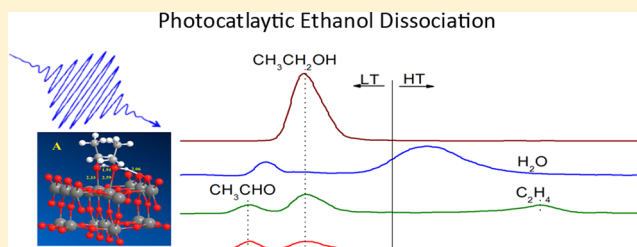
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S Supporting Information

ABSTRACT: Ethanol on TiO₂(110) has been studied using the temperature-programmed desorption (TPD), femtosecond two-photon photoemission spectroscopy (2PPE), and density functional theory (DFT) calculations. The first layer of ethanol (binds to Ti_{5c}) whose molecular state has been predicted to be more stable by DFT desorbs at 295 K. A photoinduced excited state that is associated with bridging hydroxyls has been detected at ~2.4 eV above the Fermi level on ethanol/TiO₂(110) interface using 2PPE. Detailed TPD studies show that ethanol on Ti_{5c} can be photocatalytically converted to acetaldehyde by near-band-gap excitation with the hydrogen atoms transfer to bridging-bonded oxygen sites, which is consistent with the 2PPE results. TPD results also show a low-temperature water TPD peak that seems to bind to the Ti_{5c} sites in addition to the ethylene TPD product. These results suggest that the Ti_{5c} sites on TiO₂(110) are the primary active sites for photocatalysis of ethanol on TiO₂(110), while bridging-bonded oxygen sites also play an important role, as in the case of methanol. The kinetics of photocatalyzed ethanol dissociation on TiO₂(110) has also been measured using the 2PPE technique, which is of heterogeneous nature.



1. INTRODUCTION

Alcohol chemistry on TiO₂ surfaces is a classic topic in both catalysis and surface science. Alcohol/TiO₂ systems are usually taken as models to study the mechanisms of catalytic and photocatalytic degradation of organic pollutants.^{1–3} In addition, the decomposition of simple alcohols has often been chosen to ascertain the active sites on metal oxide surfaces both experimentally^{4–6} and theoretically.^{7,8} Chemistry of ethanol on metal oxide surfaces has attracted increasing attention because ethanol is a promising renewable energy carrier for generating hydrogen and a feedstock for a possible green chemistry.^{9,10} Hydrogen production from ethanol over TiO₂-based photocatalysts has been studied in detail in the last decades.^{11–16} It is obvious that studying the chemical properties of ethanol on TiO₂ will provide microscopic insight into the photocatalytic hydrogen production process. Compared with the complexities on the powdered materials,^{9,12,17} surface chemistry on well-prepared and characterized single-crystalline substrates, for example, the prototypical rutile TiO₂(110), investigated under ultrahigh vacuum (UHV) condition might lead to the understanding of the elementary steps of the surface reactions. As a result, the thermal chemistry of ethanol on TiO₂(110) has been examined by temperature-programmed desorption (TPD),^{18–20} scanning tunneling microscopy (STM)^{21,22} and X-ray photoelectron spectroscopy (XPS).^{19,23} The photoreaction of ethanol on TiO₂(110) has also been investigated by TPD and XPS techniques.^{23,24}

The structure of TiO₂(110) surface is well understood.²⁵ It consists of alternative rows of five-coordinated Ti atoms (Ti_{5c}) and two-coordinated bridge-bonded oxygen (BBO) atoms running in the [001] direction. Surface reduction (to generate bridge-bonded oxygen vacancies, BBOv's) and bulk reduction can be easily realized by UHV annealing at moderate elevated temperature. Regarding the adsorption mode of ethanol, TPD and XPS studies have shown the dissociative adsorption on the Ti_{5c} sites at room temperature,^{19,23,24} whereas mixed molecular and dissociative adsorptions have also been proposed at liquid-nitrogen temperature using TPD and STM techniques.^{18,20,21} Density functional theory (DFT) calculations have also not reached consensus yet. Nadeem et al.'s calculations showed that the dissociative adsorption (O–H bond dissociation) of ethanol on Ti_{5c} sites is favored,^{24,26} while Besenbacher and coworkers have shown that the molecular adsorption is more stable.²¹ However, the adsorption energy of these two states is very close within the limit of DFT calculations. Thermal chemistry shows that there are mainly two reaction channels for ethanol desorption:^{18–20} the parent ethanol resulted from the recombination of ethoxy and surface hydroxyl groups desorb in the low-temperature range (LT, <400 K), while in the high-temperature range (HT, >400 K) products originated from

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recombination, dehydration, and dehydrogenation of the ethoxy groups are detected. The exceptions are Gamble et al.¹⁸ did not observe the dehydrogenation product in the high-temperature range and Kim et al.²⁰ detected the dehydration process in the low-temperature range. These divergences might arise from the differences of the sample preparation. It has been proposed that the different binding configurations are responsible for the two reaction channels. The ethoxy bound to the Ti_{5c} results in the products in the low-temperature range, whereas those bound to the BBOv's undergo chemical reactions to form products in the high-temperature range. Photo-oxidation studies suggest that ethanol will be converted to acetaldehyde and finally acetate under UV light illumination in the oxygen background.^{23,24}

Recently, we have applied the femtosecond two-photon photoemission (2PPE) spectroscopy and TPD to study the photocatalysis of methanol on $\text{TiO}_2(110)$ surface and have demonstrated that these techniques are powerful tools to study the fundamental mechanisms in photocatalysis-related process.^{27,28} An unoccupied excited state has been detected at 2.4 eV above the Fermi level (E_F) on the methanol/ $\text{TiO}_2(110)$ interface previously using 2PPE.²⁹ Later we have shown that this excited state is associated with the photocatalyzed dissociation of methanol on the Ti_{5c} sites rather than the BBOv's with the combination of 2PPE and STM,³⁰ and the photocatalyzed dissociation process to produce formaldehyde is stepwise, as confirmed by TPD experiments.²⁸ We have also found that defects on the $\text{TiO}_2(110)$ substrate can significantly change the kinetics of the photocatalyzed dissociation of methanol on Ti_{5c} sites of this surface.³¹

Here we report a combined experimental and theoretical study on the photochemistry and thermal chemistry of ethanol on the $\text{TiO}_2(110)$ surface using the TPD/2PPE methods and DFT calculations. Using the time-dependent two-photon photoemission (TD-2PPE) technique, we have observed a photoinduced excited surface state, similar to the case of methanol on $\text{TiO}_2(110)$.³⁰ TPD experiments in this work show a clear evidence of ethanol decomposition on the $\text{TiO}_2(110)$ surface. Ethanol can be photocatalytically converted to acetaldehyde, producing bridging hydroxyl groups. The amount of bridging ethoxy and terminal water (bound to the Ti_{5c} sites) increases with light illumination. Bridging hydroxyls desorb as water, while bridging ethoxy is eliminated from the $\text{TiO}_2(110)$ substrate through dehydration and recombination with a major product of ethylene. Our DFT calculations also show the ethanol molecules adsorb primarily on Ti_{5c} sites, and their molecular adsorption state is more stable than the dissociative one, in good agreement with Besenbacher et al.'s result²¹ and our own 2PPE studies. These results indicate that the photocatalytic decomposition of ethanol on $\text{TiO}_2(110)$ occurs on the Ti_{5c} sites. The photocatalyzed dissociation of ethanol complies with the fractal-like kinetics.

2. EXPERIMENTAL DETAILS

TPD and 2PPE experiments are carried out in two separate apparatus. Details of the TPD setup have been described elsewhere.^{28,32} The UHV chamber contains two parts. One is for sample preparation and characterization and the other for detection. Ar^+ ion source, LEED (low-energy electron diffraction), and AES (Auger electron spectroscopy) detector are equipped for sample preparation and characterization, respectively. The extremely low-background quadrupole mass spectrometer (Extrel, MAX-60) with electron-bombardment

ionization is employed for mass-to-charge (m/z) ratio measurement. The ionization region is housed in a liquid-nitrogen-cooled vacuum region pumped by a 500 l/s turbo molecular pump together with a liquid-nitrogen-cooled titanium sublimation pump. The background pressure of the ionization region is maintained at 1.5×10^{-12} Torr, which guarantees the high sensitivity of the mass spectrometer. An amplified 1 kHz Ti/sapphire femtosecond laser system and a frequency doubling setup constitute the optical part. The irradiating laser light in the TPD experiments had a nominal center wavelength of 400 nm, a pulse duration of ~ 60 fs, a bandwidth of ~ 20 nm, and a diameter of ~ 6 mm. $\text{TiO}_2(110)$ (Princeton Scientific, $10 \times 10 \times 1$ mm³) sample in the TPD experiments was cleaned by repeated cycles of Ar^+ ion sputtering and UHV annealing at 850 K. Sample surface quality was confirmed by AES and LEED. Density of BBOv's is $\sim 3\%$ according to the water TPD method.³³ All of the TPD experiments in this work were carried out at a ramp rate of 2 K/s.

The 2PPE experimental apparatus previously described in detail³⁴ consists of a UHV system (base pressure 5×10^{-11} mbar), which includes a sample preparation and characterization chamber and a main probing chamber as well as a Ti:Sapphire femtosecond laser system (Synergy, Femtolasers Produktions) with a repetition rate of 75 MHz. The whole probing chamber is shielded from the earth magnetism by μ -metal. The key element of this apparatus is the hemispherical electron energy analyzer (PHOIBOS 100, SPECS) for photoelectron detection. The energy and angular distribution of photoelectrons are recorded by a 2D CCD camera that facilitates the measurement of the whole photoelectrons within the energy range of interest simultaneously. Therefore, study of the kinetics of the surface reaction becomes feasible.

The $\text{TiO}_2(110)$ samples are mounted on a manipulator with five freedoms. Samples are heated through electron bombardment method and cooled by liquid nitrogen. K-type thermocouples are glued directly to the $\text{TiO}_2(110)$ surface using a ceramic adhesive (Ceramabond 503, Aremco Products, INC) to provide accurate temperature reading. The as-received $\text{TiO}_2(110)$ (Princeton Scientific, $10 \times 10 \times 1$ mm³) samples are polished on both sides to ensure maximum thermal contact. The samples are cleaned by cycles of Ar^+ sputtering (1 KeV, 15 min) and UHV annealing at 850 K (30 min). After this preparation procedure, no contamination could be detected in the AES, and a sharp (1×1) LEED pattern was observed. With more cycles of Ar^+ sputtering and UHV annealing at 850 K, the $\text{TiO}_2(110)$ became reduced with the work function (WF) to be ~ 5.2 eV, while by repeated Ar^+ sputtering and annealing at 850 K in the oxygen background (1×10^{-7} mbar) cycles the sample became oxidized and the WF increased to 5.5 to 5.8 eV.

The fundamental output of the Ti:sapphire oscillator is centered at ~ 800 nm with a pulse width of ~ 10 fs. It is converted to the second harmonic (around 400 nm, fwhm 16 nm) and then focused onto the sample (diameter ~ 100 μm). The pulse width of the 400 nm laser beam at the sample surface is ~ 28 fs. Polarization of the excitation light is rotated through a $\lambda/2$ plate before the lens. In the case of the two-photon (c. a. 400 nm) excitation from the $\text{TiO}_2(110)$ system,²⁷ the first photon excites an electron from below the E_F to above it, and the second photon excites the electron to the vacuum. The energy and angular distribution of the photoelectrons gives rise to the 2PPE spectra. Both time-resolved 2PPE (TR-2PPE) and time-dependent 2PPE (TD-2PPE) experiments can be carried out on this instrument. In the TR-2PPE experiment, one can

study the ultrafast dynamics of excited electronic states, while TD-2PPE can measure the photochemical kinetics of molecularly adsorbed surfaces. A more detailed description of the apparatus can be found in ref 34.

Ethanol (Sigma-Aldrich, HPLC grade) sample was further purified by several liquid nitrogen freeze–pump–thaw cycles. The reactants were leaked to the UHV chamber for purity check by a mass spectrometer (SRS, RGA 200). In the TPD experiments, ethanol was introduced to the $\text{TiO}_2(110)$ surface using a home-built, calibrated molecular beam doser at 110 K, whereas in the 2PPE experiments, the $\text{TiO}_2(110)$ surface was overdosed with multilayers of ethanol at 110 K through a variable leak valve doser and was then heated to 190 K according to the TPD spectra of ethanol on $\text{TiO}_2(110)$ to get rid of the extra overlayers so that a saturated first layer of ethanol on the surface was prepared. According to this work,³⁵ the saturated coverage of the first layer of ethanol on $\text{TiO}_2(110)$ is $\sim 77\%$ of the density of Ti_{5c} sites ($5.2 \times 10^{14} \text{ cm}^{-2}$), that is, 0.77 ML. In this work, the ethanol coverage was defined relative to the density of Ti_{5c} sites. After the preparation of the fresh 0.77 ML ethanol-covered $\text{TiO}_2(110)$, the substrate was then recooled to 110 K for the 2PPE experiment.

3. RESULTS AND DISCUSSIONS

3.1. Adsorption of Ethanol on $\text{TiO}_2(110)$. Figure 1 shows the typical TPD spectra of ethanol ($m/z = 45$) dosed onto the

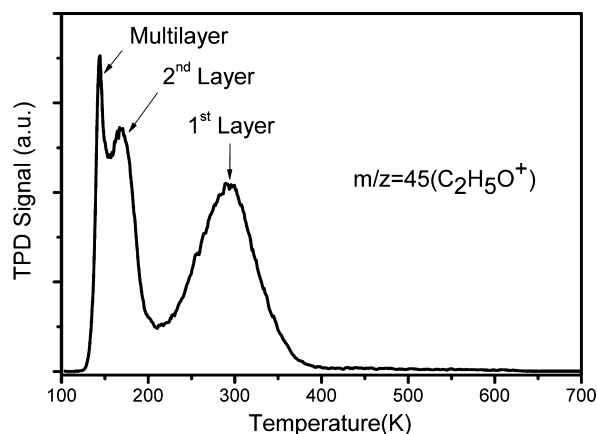
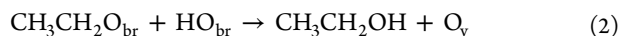


Figure 1. TPD spectra of ethanol ($m/z = 45$) that was dosed onto the $\text{TiO}_2(110)$ surface at 110 K.

slightly reduced $\text{TiO}_2(110)$ surface at 110 K. The desorption curve is similar to that of methanol.³⁶ Three desorption features peaks at 143, 168 and 295 K are observed. These peaks are due to multilayer ethanol adsorption, ethanol adsorbed on BBO sites (second layer), and ethanol adsorbed on Ti_{5c} sites (first layer), respectively.³⁵ According to a recent STM study, ethanol dissociates spontaneously at BBOv's (reaction 1).²¹ However, because of the low BBOv density in our study, recombinative desorption of ethoxy species and hydroxyls on BBO rows (reaction 2) in the high-temperature range (>400 K) is not obvious.



where O_v represents a BBOv and br denotes species adsorbed on BBO sites. The peak around 295 K is likely due to the

molecularly adsorbed ethanol on the Ti_{5c} sites, very similar to the methanol adsorption on this surface.³⁶

We have performed DFT calculations on ethanol adsorption on $\text{TiO}_2(110)$ here to validate our conclusion. The energetic and optimal structure of ethanol adsorption on $\text{TiO}_2(110)$ with no BBO defects has been determined by DFT calculations. The calculations are based on a cluster model that is identical to that in the study of methanol on $\text{TiO}_2(110)$.³⁰ Details of the cluster model are included in the Supporting Information. In brief, it consists of four layers and 286 atoms, and all the surface Ti atoms except those in the (110) surface were saturated by OH/OH₂ to maintain the coordination environment and oxidation states of Ti in bulk. BLYP functions were used in this work. Amsterdam density functional (ADF 2008) package³⁷ was used to carry out the BLYP calculations, and the double-basis set (DZ for hydrogen bond to TiO_2 and DZP for all other atoms) and the frozen-core approximation were utilized. Adsorbate coverage plays an important role in stabilizing adsorbed and dissociated configurations.³⁸ In this study, we have chosen a coverage of 0.5 ML because it is close to the actual coverage in our experiments. Dispersion interaction also has an effect on the DFT calculations. However, the results in this work do not change whether we include the dispersion interaction or not.

Figure 2A shows the optimal structure of the molecular state of ethanol adsorbed on the $\text{TiO}_2(110)$ surface (whole optimized configuration is included in the Supporting Information). Like methanol, the two ethanol molecules adsorbed on top of the Ti_{5c} sites adjacently on $\text{TiO}_2(110)$ surface, forming an intermolecular hydrogen bond and an adsorbate–substrate hydrogen bond. The structure of the substrate is very close to that of the bare surface. The longer Ti–O distance²⁶ together with the lower diffuse barrier along Ti trough²¹ suggests ethanol molecules bind weakly to the $\text{TiO}_2(110)$ surface compared with ethoxy. According to the calculation, the ethanol molecule is primarily adsorbed on the Ti_{5c} site as methanol and its O–H bond dissociation (with the hydroxyl H atom transferred to the nearby BBO site, Figure 2B) on $\text{TiO}_2(110)$ is endothermic by 5.14 kcal/mol (the value is 4.89 kcal/mol when dispersion interaction is included), while that for methanol is 2.97 kcal/mol. This result is also in fairly good agreement with the DFT results obtained by Besenbacher and coworkers.²¹ Given the fact that the dissociation of methanol on Ti_{5c} is not spontaneous at 110 K,³⁰ we can confidently say that ethanol dissociation on $\text{TiO}_2(110)$ should also not be spontaneous at this temperature. This means that ethanol should be adsorbed molecularly on Ti_{5c} sites at liquid-nitrogen temperature.

After exposure of the ethanol-covered $\text{TiO}_2(110)$ to the laser light near 400 nm, significant changes have been observed. A photoinduced electronic excited state has been detected in 2PP spectra. Acetaldehyde, ethylene, and water have been identified using TPD. The results, which unambiguously suggest the photocatalyzed dissociation of ethanol on $\text{TiO}_2(110)$, will be shown in the following parts.

3.2. 2PPE Results. Both bare and ethanol-covered $\text{TiO}_2(110)$ have been studied using the 2PPE method. Figure 3 shows a typical 2PPE spectrum for bare and 0.77 ML ethanol-covered oxidized $\text{TiO}_2(110)$ surface. The bottom X axis represents the final-state energy relative to the E_F , while the top X axis indicates the energy of any intermediate state before the absorption of the second photon. The weak 2PPE intensity along with the high WF of the bare surface suggests few BBOv's on the surface.³⁹ In the experiment, the ethanol-covered

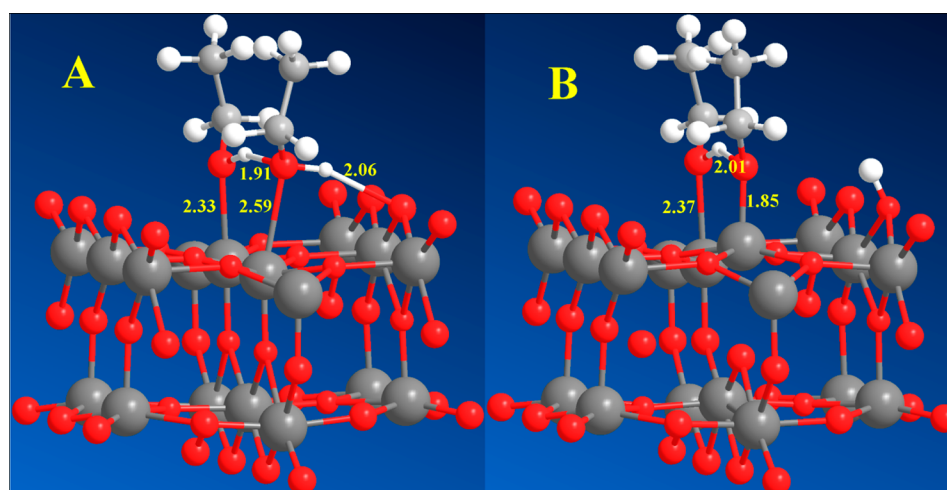


Figure 2. Optimal structure of molecular (A) and O–H-dissociated (B) state of ethanol adsorption on Ti_{5c} sites of $\text{TiO}_2(110)$. Only the local structures of the surface region are shown. The full cluster model is given in the Supporting Information.

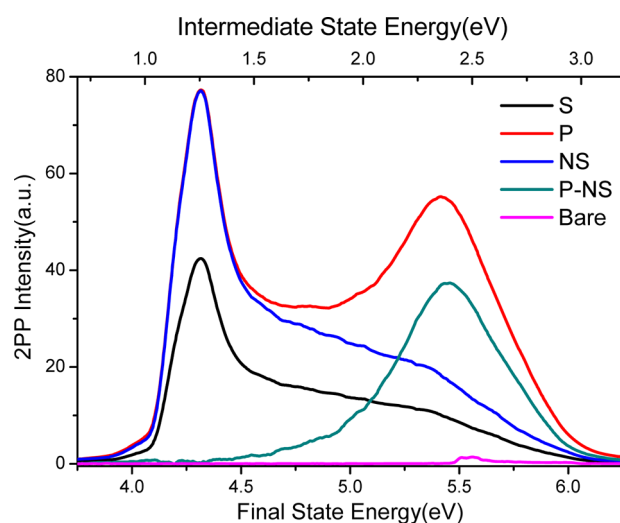


Figure 3. 2PP spectra for the bare and ethanol-covered oxidized $\text{TiO}_2(110)$ surface. The spectra for ethanol-adsorbed $\text{TiO}_2(110)$ surface were measured with both p-polarized (P) and s-polarized (S) light after the fresh ethanol/ $\text{TiO}_2(110)$ surface was illuminated by the p-polarized light (402.5 nm, flux 1.4×10^{21} photons/ cm^2/s) for more than 1000 s. P-NS stood for the pure excited resonance signal that was obtained by subtracting the normalized s-polarized data (NS) from the p-polarized data. The signal in these spectra was integrated from -5° to $+5^\circ$. The energies were measured with respect to the Fermi level.

$\text{TiO}_2(110)$ surface was illuminated by a 402.5 nm femtosecond laser beam with the power of 68 mW (flux 1.4×10^{21} photons/ cm^2/s) for more than 1000 s. The 2PPE intensity becomes much stronger, similar to the case of water and methanol.^{39,40} Except the secondary electron signal (the low-energy peak), the 2PPE spectrum measured with p-polarized light is very different from that with s-polarized light. An additional excited resonance feature at ~ 2.4 eV above E_F is observed with p-polarized light, similar to the case of methanol on $\text{TiO}_2(110)$.²⁹ The excited resonance signal appears in the two-photon photoemission and not in one-photon photoemission, suggesting that the excited resonance signal comes from an initially unoccupied intermediate state. The excited resonance signal reaches its maximum when 0.77 ML ethanol is adsorbed on the

$\text{TiO}_2(110)$ surface, implying that it is closely related to the first layer adsorption on this surface, that is, on the Ti_{5c} sites.

To investigate the origin of the excited resonance feature, we have also performed TD-2PPE measurement. For a fresh 0.77 ML ethanol-adsorbed $\text{TiO}_2(110)$ surface, we measured a series of time-dependent 2PPE spectrum with an exposure time of 1 s for each spectrum, immediately after the laser light starts to shine on the surface. Figure 4A shows a few 2PPE spectrum for the 0.77 ML ethanol-covered $\text{TiO}_2(110)$ surface taken after different durations of light illumination. (A 3D time-dependent 2PPE spectrum with a series of light illumination time can be found in Figure S2 in the Supporting Information.) The most interesting observation is that the 2PPE spectrum measured at

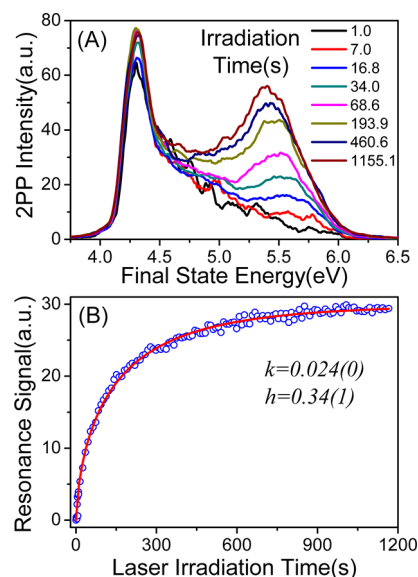


Figure 4. (A) Typical 2PP spectra after various exposure of the ethanol-covered oxidized $\text{TiO}_2(110)$ to the femtosecond laser beam (402.5 nm, flux 1.4×10^{21} photons/ cm^2/s). Each spectrum was acquired with a CCD exposure time of 1 s. The signal in these spectra was integrated from -5° to $+5^\circ$. (B) Time-dependent signal of the 2PPE excited resonance feature of ethanol/ $\text{TiO}_2(110)$ surface. The signal was integrated between 4.9 and 6.1 eV from Figure S2A in the Supporting Information.

the first second of laser illumination is very different from those measured after a longer period of laser exposure. Clearly, the excited resonance feature around 5.5 eV increases quickly as the 402.5 nm light exposure time increases. At the shortest exposure time, the 2PPE spectrum shows little of the resonance feature, suggesting that the excited resonance feature does not exist on the fresh ethanol-adsorbed TiO₂(110) surface, whereas after longer time exposure the resonance feature becomes very pronounced and finally saturates. The excited resonance peak position seems to shift from ~5.7 eV at the beginning to ~5.4 eV in the end as the laser illumination time increases. Obviously, this photoinduced electronic excited resonance is due to electronic structure change of the ethanol/TiO₂(110) surface.

Unfortunately, the exact nature of the excited state is not known immediately because of the difficulties of DFT in calculating the excited states. We have performed a series of 2PPE experiments to speculate the possible structures that support the excited state. Bridging hydroxyls do not produce this state, neither does terminal (bound to Ti_{5c}) RO (e.g., H₂O, CH₃OH, C₂H₅OH, C₃H₇OH, CH₃OCH₃) or RN (e.g., NH₃) or RS (e.g., CH₃CH₂SH). However, on the TiO₂(110) surface with coadsorbed bridging hydroxyls and terminal RO/RN, 2PPE has detected this excited state, whereas the coexistence of bridging hydroxyls and terminal RS does not lead to that state. Hydroxyls can form hydrogen bond with terminal RO and RN but cannot with terminal RS. Therefore, it seems the interaction between the terminal species and bridging hydroxyls through hydrogen bond plays an important role in the formation of the excited state. However, further experimental and theoretical analysis are urgently needed to clarify what the excited state is.

Although the physical nature of the excited state on the alcohol/TiO₂(110) interface remains unclear, we have learnt that the bridging hydroxyls are necessary for the occurrence of this state. Thus the total absence of the excited resonance signal at the very beginning of light illumination on ethanol/TiO₂(110) interface suggests negligible bridging hydroxyls at that time. This implies that ethanol adsorbed on Ti_{5c} sites is not dissociated, which is consistent with TPD and DFT results in the former text. With the increase in light exposure, the excited resonance signal becomes more and more intense, indicating on the BBO sites that there are more and more hydroxyl groups that are likely due to photocatalytic dissociation of ethanol on TiO₂(110). We have studied the effect of extent of the substrate reduction on the photochemistry of ethanol on TiO₂(110),⁴¹ and find that the apparent photoinduced phenomena are similar except the reaction rate. This is also similar to methanol.³¹ 2PPE measurements of the photochemistry of ethanol on reduced TiO₂(110) are shown in Figure S2 in Supporting Information.

Because the rising excited state on ethanol/TiO₂(110) is probably associated with the photocatalyzed dissociation of ethanol, the evolution of the excited resonance signal in the 2PPE experiment should reflect the kinetics of this photocatalyzed process. By integrating the 2PPE spectrum in Figure S2A in the Supporting Information between 4.9 and 6.1 eV, the time-dependent excited resonance signal is obtained and shown in Figure 4B. Given the effect of trapping and detrapping of the photoexcited charge carriers (electrons and holes) on the photocatalyzed chemistry on TiO₂(110),⁴² we chose a fractal like kinetic model to simulate the experimental data^{43,44}

$$I = I_0 \left(1 - \exp \left(- \frac{k_0}{1-h} t^{1-h} \right) \right) \quad (3)$$

where k_0 is the rate at $t = 1$ s and the h parameter is equal to $1 - d_s/2$, where d_s is the spectral dimension of the heterogeneous reaction media. The rate coefficient can be written as

$$k = k_0 t^{-h} \quad (4)$$

From Figure 4B, one can see that this fractal model fits the kinetics of the rising 2PPE resonance feature very well. This suggests that the photochemistry process involved is of heterogeneous nature.

3.3. TPD Results. TPD has been used in view of unraveling the surface chemical process. All possible products have been collected, and no products with $m/e > 46$ have been detected. After TPD to 750 K there is no detectable carbon signal in AES on the TiO₂ substrate. Figure 5 shows all detectable desorption

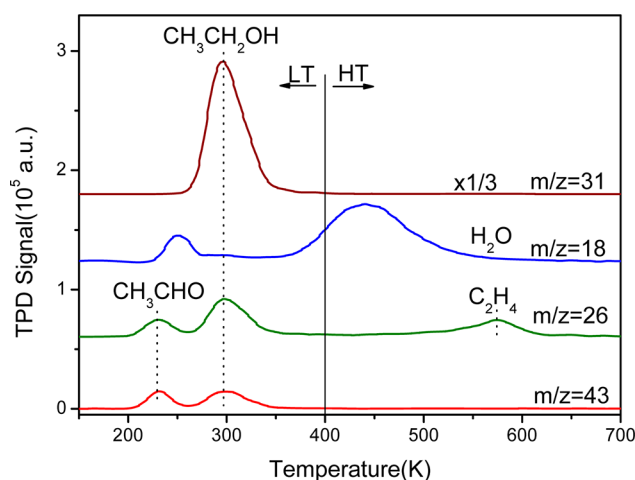


Figure 5. Typical TPD spectrum after 0.35 ML ethanol-covered TiO₂(110) has been illuminated by laser light (400 nm, flux 2.6×10^{18} photons/cm²/s) for 20 min. All detectable products with a typical tracing mass to charge ratio are shown here. The profiles are offset vertically for clarity.

products when 0.35 ML ethanol-covered TiO₂(110) has been illuminated by laser light (400 nm, 460 mW, flux 2.6×10^{18} photons/cm²/s) for 20 min. There are four reaction products with the representative tracing mass-to-charge ratio of 31, 43, 18, and 26. Similar to thermal chemistry studies,^{18–20,35} two distinct desorption regions have been observed, that is, LT below and HT above 400 K. In the low-temperature region, all of the traced masses have desorption features, whereas in the high-temperature region, there is no desorption signals for mass 43.

Mass 31 and 45 have been used to follow ethanol desorption. These two desorption profiles are exactly the same, indicating they are simply the fragments from parent ethanol decomposition in the ionizer region. Figure 6 shows ethanol ($m/z = 31$) TPD spectra as a function of laser light illumination to 0.35 ML ethanol-adsorbed TiO₂(110). The main TPD feature around 310 K is due to ethanol species adsorption at Ti_{5c} sites. It is evident that the 310 K TPD peak shifts toward lower temperature and the whole desorption profile becomes narrower with increasing light illumination, resulting in the monotonically decrease in the total TPD signal. The shrink of the high-temperature part of the ethanol desorption peak is

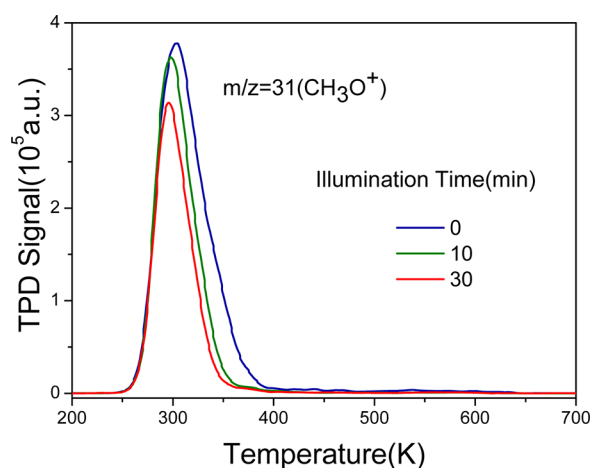


Figure 6. TPD spectrum ($m/z = 31$) of 0.35 ML ethanol dosed onto the slightly reduced $\text{TiO}_2(110)$ surface at 110 K after different time period of laser light (400 nm, flux 2.6×10^{18} photons/ cm^2/s) illumination.

ascribed to the downward shift of the TPD profile due to the increase in bridging hydroxyl density from photocatalytic splitting of ethanol.²⁸ Without illumination, the recombinative desorption signal is $\sim 2\%$ of that of monolayer. There are 0.03 ML ethoxy on BBO rows (BBOv coverage 0.03 ML) and 0.32 ML ethanol on Ti_{5c} sites. Therefore, the absolute amount of recombination ethanol is 0.0064 ML, which constitutes only 1/5 of the bridging ethoxy. The majority of the rest are converted to ethylene. Detailed results will be shown in the following text.

The ethanol signal decreases with light illumination, while the TPD signal for mass 43, 18, and 26 increases. Figure 7

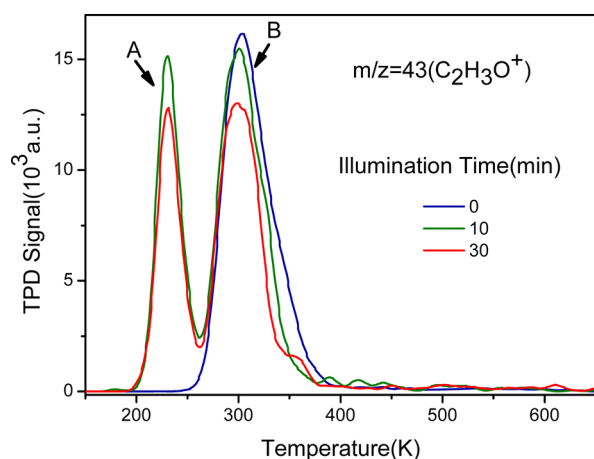


Figure 7. Typical TPD spectra collected at $m/z = 43$ ($\text{C}_2\text{H}_3\text{O}^+$) following different laser irradiation times (400 nm, flux 2.6×10^{18} photons/ cm^2/s). The $m/z = 43$ ($\text{C}_2\text{H}_3\text{O}^+$) signal has two components: the ion-fragment signal of the photocatalyzed acetaldehyde (CH_3CHO) product (A) as well as the ion-fragment signals of the parent $\text{C}_2\text{H}_5\text{OH}$ molecule (B).

shows the evolution of the TPD signal for mass 43 with a series of illumination time. The signal around 310 K (labeled as B) originates from the fragment of ethanol as the desorption profile is identical to both mass 45 and 31. An additional desorption feature at 234 K (labeled as A) grows in after the shortest light illumination time and increases rapidly to its maximum within 10 min, followed by a slow decrease, which is

likely due to photodesorption, similar to the case of methanol.²⁸ Analysis of TPD signals at mass 43, 29, and 15 suggests that this peak is due to acetaldehyde desorption. This can be further confirmed by the TPD spectra of acetaldehyde directly dosed onto $\text{TiO}_2(110)$ surface.⁴⁵ To produce acetaldehyde, an ethanol molecule has to release a hydroxyl H and an α -H. The released hydrogen atoms are most probably transferred to BBO sites, which has been proved in the photocatalytic chemistry of methanol on $\text{TiO}_2(110)$ ^{28,46,47} and also confirmed by water TPD studies in the present work.

Similar to the increase in acetaldehyde product, the TPD signal for $m/z = 18$ also increases with laser irradiation times (Figure 8). Without light illumination, two desorption peaks

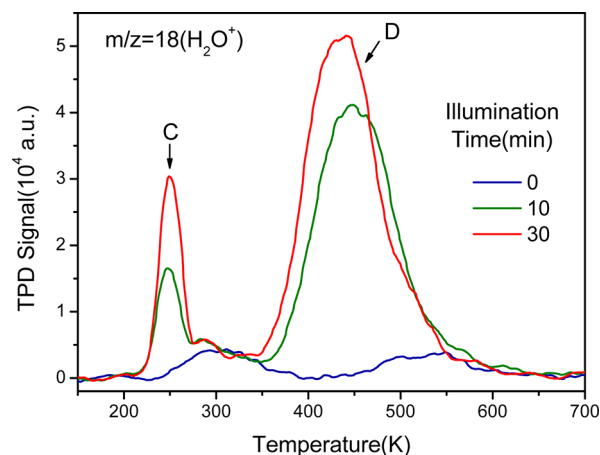
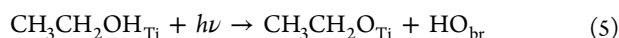


Figure 8. TPD spectrum for $m/z = 18$ as a function of light illumination (400 nm, flux 2.6×10^{18} photons/ cm^2/s) after 0.35 ML ethanol was dosed onto the slightly reduced $\text{TiO}_2(110)$ surface at 110 K.

around 300 and 520 K, respectively, are observed. The former is due to molecularly adsorbed water (at Ti_{5c} sites)⁴⁸ from UHV residual/impurities in ethanol reagent, whereas the latter is attributed to the recombinative desorption of bridging hydroxyls,⁴⁹ which are formed by spontaneous dissociation of water/ethanol. The magnitude of the TPD signals in the high-temperature region (labeled as D) increases with the illumination time and the peak positions shift downward. This kind of line-shape progression style is common for bridging hydroxyls recombination TPD from $\text{TiO}_2(110)$ with various bridging hydroxyl density,^{50,51} indicating the TPD signals in this temperature range arise from bridging hydroxyls produced by splitting of ethanol at Ti_{5c} sites. This implies hydrogen atoms from ethanol dissociation transfer to the BBO sites, which is in accord with the 2PPE study. The transfer of the released hydrogen atoms to the BBO sites leads to the appearance of the excited state detected in the 2PPE spectrum.

The very close adsorption energy of molecular and dissociated states of ethanol at Ti_{5c} sites^{24,26} together with the direct observation of coexistence of these two states on a $\text{TiO}_2(110)$ substrate with the substrate temperature slightly higher than this study by STM²¹ suggest the cleavage of O–H bond is easy. As ethanol originally adsorbs molecularly on Ti_{5c} sites, the breaking of O–H is a photoinduced process in our study (reaction 5). In contrast with O–H, the dissociation of the C–H bond needs much more energy. It is a photocatalyzed process (reaction 6), as in the case of methanol.^{28,46}



where Ti denotes species adsorb on Ti_{5c} and $h\nu$ stands for a photon. The photocatalyzed dehydrogenation of ethanol on Ti_{5c} is most likely a stepwise process, similar to the case of methanol.²⁸

Aside from the recombinative desorption of bridging hydroxyls, another water desorption feature grows in around 250 K (labeled as C) when the laser light starts to illuminate the ethanol-covered $\text{TiO}_2(110)$. Such a low-temperature desorption feature can only be associated with water species on Ti_{5c} sites. However, hydrogen atoms released from ethanol dissociation have been transferred to the BBO sites. The relative low desorption temperature of state C (20 K lower than the typical water monolayer desorption from clean $\text{TiO}_2(110)$ ⁴⁸) resembles water desorption from $\text{TiO}_2(110)$ with coadsorbed water and methanol,³⁶ where the downward shift of the monolayer water desorption temperature is accounted for by the displacement of methanol molecules on Ti_{5c} sites for bridging hydroxyls. This kind of displacement has also been reported on hydroxylated TiO_2 powders covered by alcohols including ethanol.^{52–54} However, we have detected negligible displacement products in a control experiment where ethanol and bridging hydroxyls coadsorb on the $\text{TiO}_2(110)$ surface. Therefore, it is not immediately clear where the water species on Ti_{5c} sites originate from, and further studies are needed to clarify this point. These works are now under consideration in our laboratory.

Possible carbon-containing products desorbing in the high-temperature range have also been measured. A careful comparison of the crack pattern (mass 25, 26, 27, 28) suggests the desorption of ethylene at ~600 K. Figure 9 shows the TPD

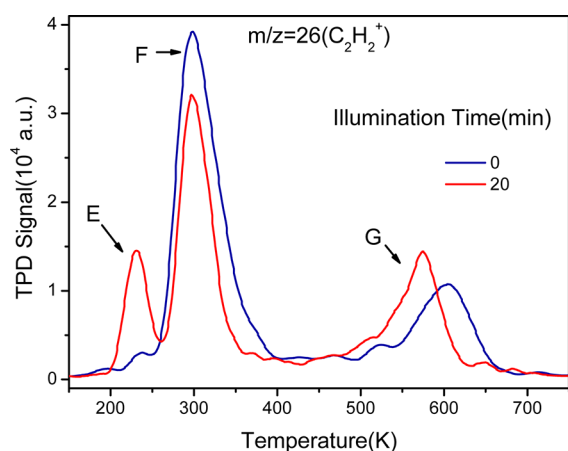


Figure 9. TPD spectrum for $m/z = 26$ as a function of light illumination (400 nm, flux 2.6×10^{18} photons/cm²/s) after 0.35 ML ethanol was dosed onto the slightly reduced $\text{TiO}_2(110)$ surface at 110 K. Acetaldehyde fragment (E), ethanol fragment (F), and ethylene fragment (G) contribute to this spectrum.

spectrum for $m/z = 26$ as a function of light illumination. There are three desorption peaks labeled E, F, and G, which correspond to acetaldehyde, ethanol, and ethylene fragments, respectively. Ethylene is produced by β -H elimination of the bridging ethoxy through thermal reaction.^{18,19} There are ethoxy species originally residing on bridging oxygen rows through spontaneous dissociation of ethanol at oxygen vacancies before

light illumination. These ethoxy desorb at ~600 K as ethylene and ethanol during the heating process of TPD experiment, with an ethylene-to-ethanol ratio of 4:1. The 400 nm light obviously has an effect on the ethylene production. After 400 nm light illumination, the peak position shifts downward and the total intensity is enhanced. A possible explanation is as follows: Bridging hydroxyls from photocatalyzed splitting of ethanol can desorb as water through recombination, leaving BBOv's. This will result in insufficient hydroxyls to remove all of the $\text{CH}_3\text{CH}_2\text{O}_{\text{Ti}}$, an intermediate product to generate acetaldehyde. These residual $\text{CH}_3\text{CH}_2\text{O}_{\text{Ti}}$ might migrate to the BBOv's and finally desorb predominantly as ethylene during the post-irradiation TPD measurements.

So far, the photochemistry and the resulted thermal chemistry of ethanol on $\text{TiO}_2(110)$ have been carefully studied. Clearly, ethanol molecules adsorbed on Ti_{5c} sites are converted to ethoxy first and eventually to acetaldehyde through a photocatalytic reaction, with the released hydrogen atoms transferring to BBO sites, forming bridging hydroxyls. Bridging ethoxy could be formed in the heating process of the TPD experiments and finally desorb by major dehydration and minor recombination during the postirradiation TPD.

4. CONCLUSIONS

In this work, photocatalysis-TPD, 2PPE methods, as well as DFT calculations have been utilized to study the photocatalytic and related thermal chemistry of ethanol on the $\text{TiO}_2(110)$ surface. Experimental and theoretical results reveal that ethanol adsorbs molecularly on the Ti_{5c} sites of $\text{TiO}_2(110)$ surface. A photoinduced excited state at ~2.4 eV above the Fermi level of ethanol/ $\text{TiO}_2(110)$ interface has been detected. Control experiments indicate that the photoinduced excited state is related to bridging hydroxyls generated from ethanol photocatalytic dissociation. More detailed TPD experiment shows dehydrogenation of ethanol on Ti_{5c} , yielding acetaldehyde and bridging hydroxyls. Both the cleavage of O–H as well as the α C–H breaking is photoinduced in this process. In addition, photolysis-TPD experiments show a low-temperature water peak as well as high-temperature ethylene products from the photocatalysis of ethanol on $\text{TiO}_2(110)$. From these results, it is clear that the excited state observed in the 2PPE spectra is associated with the dissociation of ethanol on the Ti_{5c} sites. This provides us a unique tool to monitor photocatalytic kinetics of ethanol on TiO_2 . Time-dependent 2PPE kinetic measurement of the photocatalyzed dissociation of ethanol on $\text{TiO}_2(110)$ suggests that photocatalyzed dissociation of ethanol on $\text{TiO}_2(110)$ is of heterogeneous nature, similar to the case of methanol.

■ ASSOCIATED CONTENT

Supporting Information

Details of the cluster model, whole optimized structure of the molecular and dissociated configuration, and the 3D time-dependent 2PPE spectra for 0.77 ML ethanol-covered oxidized and reduced $\text{TiO}_2(110)$ with a series of light illumination time. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

[§]Zhibo Ma and Qing Guo made similar contributions to this work.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Linsebigler, A. L.; Lu, G. Q.; Yates, J. T. Photocatalysis on TiO₂ Surfaces - Principles, Mechanisms, and Selected Results. *Chem Rev* **1995**, *95*, 735–758.
- (2) Fujishima, A.; Rao, T. N.; Tryk, D. A. Titanium Dioxide Photocatalysis. *J. Photochem. Photobiol., C* **2000**, *1*, 1–21.
- (3) Fujishima, A.; Zhang, X.; Tryk, D. A. TiO₂ Photocatalysis and Related Surface Phenomena. *Surf. Sci. Rep.* **2008**, *63*, 515–582.
- (4) Thompson, T. L.; Yates, J. T. TiO₂-Based Photocatalysis: Surface Defects, Oxygen and Charge Transfer. *Top. Catal.* **2005**, *35*, 197–210.
- (5) Pang, C. L.; Lindsay, R.; Thornton, G. Chemical Reactions on Rutile TiO₂(110). *Chem Soc Rev* **2008**, *37*, 2328–2353.
- (6) Dohnalek, Z.; Lyubinetsky, I.; Rousseau, R. Thermally-Driven Processes on Rutile TiO₂(110)-(1 × 1): A Direct View at the Atomic Scale. *Prog. Surf. Sci.* **2010**, *85*, 161–205.
- (7) Bates, S. P.; Kresse, G.; Gillan, M. J. The Adsorption and Dissociation of ROH Molecules on TiO₂(110). *Surf. Sci.* **1998**, *409*, 336–349.
- (8) de Armas, R. S.; Oviedoaaa, J.; San Miguel, M. A.; Sanz, J. F. Methanol Adsorption and Dissociation on TiO₂(110) from First Principles Calculations. *J. Phys. Chem. C* **2007**, *111*, 10023–10028.
- (9) Idriss, H. Ethanol Reactions over the Surfaces of Noble Metal/Cerium Oxide Catalysts. *Platinum Metals Rev.* **2004**, *48*, 105–115.
- (10) Haryanto, A.; Fernando, S.; Murali, N.; Adhikari, S. Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review. *Energy Fuels* **2005**, *19*, 2098–2106.
- (11) Bamwenda, G. R.; Tsubota, S.; Nakamura, T.; Haruta, M. Photoassisted Hydrogen-Production From A Water-Ethanol Solution - A Comparison Of Activities Of Au-TiO₂ And Pt-TiO₂. *J. Photochem. Photobiol., A* **1995**, *89*, 177–189.
- (12) Idriss, H.; Seebauer, E. G. Reactions of Ethanol Over Metal Oxides. *J. Mol. Catal. A: Chem.* **2000**, *152*, 201–212.
- (13) Llorca, J.; Homs, N.; Sales, J.; de la Piscina, P. R. Efficient Production of Hydrogen Over Supported Cobalt Catalysts from Ethanol Steam Reforming. *J. Catal.* **2002**, *209*, 306–317.
- (14) Stratakis, N.; Antoniadou, M.; Dracopoulos, V.; Lianos, P. Visible-Light Photocatalytic Hydrogen Production from Ethanol-Water Mixtures Using A Pt-CdS-TiO₂ Photocatalyst. *Catal. Today* **2010**, *151*, 53–57.
- (15) Murdoch, M.; Waterhouse, G. I. N.; Nadeem, M. A.; Metson, J. B.; Keane, M. A.; Howe, R. F.; Llorca, J.; Idriss, H. The Effect of Gold Loading and Particle Size on Photocatalytic Hydrogen Production from Ethanol Over Au/TiO₂ Nanoparticles. *Nat. Chem.* **2011**, *3*, 489–492.
- (16) Nadeem, M. A.; Murdoch, M.; Waterhouse, G. I. N.; Metson, J. B.; Keane, M. A.; Llorca, J.; Idriss, H. Photoreaction of Ethanol on Au/TiO₂ Anatase: Comparing the Micro to Nanoparticle Size Activities of the Support for Hydrogen Production. *J. Photochem. Photobiol., A* **2010**, *216*, 250–255.
- (17) Nadeem, A. M.; Waterhouse, G. I. N.; Idriss, H. The Reactions of Ethanol on TiO₂ and Au/TiO₂ Anatase Catalysts. *Catal. Today* **2012**, *182*, 16–24.
- (18) Gamble, L.; Jung, L. S.; Campbell, C. T. Decomposition and Protonation of Surface Ethoxys on TiO₂(110). *Surf. Sci.* **1996**, *348*, 1–16.
- (19) Farfan-Arribas, E.; Madix, R. J. Role of Defects in the Adsorption of Aliphatic Alcohols on the TiO₂(110) Surface. *J. Phys. Chem. B* **2002**, *106*, 10680–10692.
- (20) Kim, Y.; Kay, B.; White, J.; Dohnalek, Z. Alcohol Chemistry on Rutile TiO₂ (110): The Influence of Alkyl Substituents on Reactivity and Selectivity. *J. Phys. Chem. C* **2007**, *111*, 18236–18242.
- (21) Hansen, J. Ø.; Huo, P.; Martinez, U.; Lira, E.; Wei, Y. Y.; Streber, R.; Lægsgaard, E.; Hammer, B.; Wendt, S.; Besenbacher, F. Direct Evidence for Ethanol Dissociation on Rutile TiO₂(110). *Phys. Rev. Lett.* **2011**, *107*, 136102.
- (22) Huo, P.; Hansen, J. O.; Martinez, U.; Lira, E.; Streber, R.; Wei, Y. Y.; Lægsgaard, E.; Hammer, B.; Wendt, S.; Besenbacher, F. Ethanol Diffusion on Rutile TiO₂(110) Mediated by H Adatoms. *J. Phys. Chem. Lett.* **2012**, *3*, 283–288.
- (23) Jayaweera, P. M.; Quah, E. L.; Idriss, H. Photoreaction of Ethanol on TiO₂(110) Single-Crystal Surface. *J. Phys. Chem. C* **2007**, *111*, 1764–1769.
- (24) Nadeem, A. M.; Muir, J. M. R.; Connelly, K. A.; Adamson, B. T.; Metson, B. J.; Idriss, H. Ethanol Photo-Oxidation on a Rutile TiO₂(110) Single Crystal Surface. *Phys. Chem. Chem. Phys.* **2011**, *13*, 7637–7643.
- (25) Diebold, U. The Surface Science of Titanium Dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53–229.
- (26) Muir, J. N.; Choi, Y.; Idriss, H. Computational Study of Ethanol Adsorption and Reaction Over Rutile TiO₂(110) Surfaces. *Phys. Chem. Chem. Phys.* **2012**, *14*, 11910–11919.
- (27) Zhou, C.; Ma, Z.; Ren, Z.; Wodtke, A. M.; Yang, X. Surface Photochemistry Probed by Two-Photon Photoemission Spectroscopy. *Energy Environ. Sci.* **2012**, *5*, 6833–6844.
- (28) 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 TiO₂(110). *J. Am. Chem. Soc.* **2012**, *134*, 13366–13373.
- (29) Li, B.; Zhao, J.; Onda, K.; Jordan, K. D.; Yang, J. L.; Petek, H. Ultrafast Interfacial Proton-Coupled Electron Transfer. *Science* **2006**, *311*, 1436–1440.
- (30) Zhou, C. Y.; Ren, Z. F.; Tan, S. J.; Ma, Z. B.; Mao, X. C.; Dai, D. X.; Fan, H. J.; Yang, X. M.; LaRue, J.; Cooper, R.; et al. Site-Specific Photocatalytic Splitting of Methanol on TiO₂(110). *Chem. Sci.* **2010**, *1*, 575–580.
- (31) Zhou, C.; Ma, Z.; Ren, Z.; Mao, X.; Dai, D.; Yang, X. Effect of Defects on Photocatalytic Dissociation of Methanol on TiO₂(110). *Chem. Sci.* **2011**, *2*, 1980–1983.
- (32) Ren, Z. F.; Guo, Q.; Xu, C. B.; Yang, W. S.; Xiao, C. L.; Dai, D. X.; Yang, X. M. Surface Photocatalysis-TPD Spectrometer for Photochemical Kinetics. *Chin. J. Chem. Phys.* **2012**, *25*, 507–512.
- (33) Henderson, M. A. The Interaction of Water with Solid Surfaces: Fundamental Aspects Revisited. *Surf. Sci. Rep.* **2002**, *46*, 1–308.
- (34) Ren, Z. F.; Zhou, C. Y.; Ma, Z. B.; Xiao, C. L.; Mao, X. C.; Dai, D. X.; LaRue, J.; Cooper, R.; Wodtke, A. M.; Yang, X. M. A Surface Femtosecond Two-Photon Photoemission Spectrometer for Excited Electron Dynamics and Time-Dependent Photochemical Kinetics. *Chin. J. Chem. Phys.* **2010**, *23*, 255–261.
- (35) Li, Z.; Smith, R. S.; Kay, B. D.; Dohnalek, Z. Determination of Absolute Coverages for Small Aliphatic Alcohols on TiO₂(110). *J. Phys. Chem. C* **2011**, *115*, 22534–22539.
- (36) Henderson, M. A.; Otero-Tapia, S.; Castro, M. E. The Chemistry of Methanol on the TiO₂ (110) Surface: The Influence of Vacancies and Coadsorbed Species. *Faraday Discuss.* **1999**, *313*–329.
- (37) Velde, G. T.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; Van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J. Comput. Chem.* **2001**, *22*, 931–967.
- (38) Zhao, J.; Yang, J. L.; Petek, H. Theoretical Study of the Molecular and Electronic Structure of Methanol on a TiO₂(110) Surface. *Phys. Rev. B* **2009**, *80*, 235416–235426.

- (39) Onda, K.; Li, B.; Petek, H. Two-Photon Photoemission Spectroscopy of $\text{TiO}_2(110)$ Surfaces Modified by Defects and O_2 or H_2O Adsorbates. *Phys. Rev. B* **2004**, *70*, 045415–045126.
- (40) Li, B. Two-Photon Photoemission Spectroscopy of Wet Electron State and Femtosecond Electron Dynamics on TiO_2 Surfaces. Doctoral Thesis, University of Pittsburgh, 2006.
- (41) Ma, Z. B.; Zhou, C. Y.; Mao, X. C.; Ren, Z. F.; Dai, D. X.; Yang, X. M. Kinetics and Dynamics of Photocatalyzed Dissociation of Ethanol on $\text{TiO}_2(110)$. *Chin. J. Chem. Phys.* **2013**, *26*, 1–7.
- (42) Thompson, T. L.; Yates, J. T. Control of a Surface Photochemical Process by Fractal Electron Transport Across the Surface: O_2 Photodesorption from $\text{TiO}_2(110)$. *J. Phys. Chem. B* **2006**, *110*, 7431–7435.
- (43) Kopelman, R. Rate Processes on Fractals: Theory, Simulations, and Experiments. *J. Stat. Phys.* **1986**, *42*, 185–200.
- (44) Kopelman, R. Fractal Reaction Kinetics. *Science* **1988**, *241*, 1620–1626.
- (45) Zehr, R. T.; Henderson, M. A. Acetaldehyde Photochemistry on $\text{TiO}_2(110)$. *Surf. Sci.* **2008**, *602*, 2238–2249.
- (46) Shen, M.; Henderson, M. A. Identification of the Active Species in Photochemical Hole Scavenging Reactions of Methanol on TiO_2 . *J. Phys. Chem. Lett.* **2011**, *2*, 2707–2710.
- (47) Shen, M. M.; Henderson, M. A. Role of Water in Methanol Photochemistry on Rutile $\text{TiO}_2(110)$. *J. Phys. Chem. C* **2012**, *116*, 18788–18795.
- (48) Henderson, M. A. An HREELS and TPD Study of Water on $\text{TiO}_2(110)$: The Extent of Molecular Versus Dissociative Adsorption. *Surf. Sci.* **1996**, *355*, 151–166.
- (49) Zehr, R. T.; Henderson, M. A. Influence of O_2 Induced Surface Roughening on the Chemistry of Water on $\text{TiO}_2(110)$. *Surf. Sci.* **2008**, *602*, 1507–1516.
- (50) Lane, C. D.; Petrik, N. G.; Orlando, T. M.; Kimmel, G. A. Electron-Stimulated Oxidation of Thin Water Films Adsorbed on $\text{TiO}_2(110)$. *J. Phys. Chem. C* **2007**, *111*, 16319–16329.
- (51) Petrik, N. G.; Kimmel, G. A. Nonthermal Water Splitting on Rutile TiO_2 : Electron-Stimulated Production of H_2 and O_2 in Amorphous Solid Water Films on $\text{TiO}_2(110)$. *J. Phys. Chem. C* **2009**, *113*, 4451–4460.
- (52) Suda, Y.; Morimoto, T.; Nagao, M. Adsorption of Alcohols on Titanium-Dioxide (Rutile) Surface. *Langmuir* **1987**, *3*, 99–104.
- (53) Taylor, E. A.; Griffin, G. L. Product Selectivity during CH_3OH Decomposition on TiO_2 Powders. *J. Phys. Chem.* **1988**, *92*, 477–481.
- (54) Carrizosa, I.; Munuera, G.; Castanar, S. Study of Interaction of Aliphatic-Alcohols with TiO_2 0.3. Formation of Alkyl-Titanium Species during Methanol Decomposition. *J. Catal.* **1977**, *49*, 265–277.