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Photoinduced Decomposition of Formaldehyde on Rutile TiO$_2$(100)-(1×1) $^{\dagger}$

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We have investigated the photoinduced decomposition of formaldehyde (CH$_2$O) on a rutile TiO$_2$(100)-(1×1) surface at 355 nm using temperature-programmed desorption. Products, formate (HCOO$^-$), methyl radical (CH$_3$), ethylene (C$_2$H$_4$), and methanol (CH$_3$OH) have been detected. The initial step in the decomposition of CH$_2$O on the rutile TiO$_2$(100)-(1×1) surface is the formation of a dioxymethylene intermediate in which the carbonyl O atom of CH$_2$O is bound to a Ti atom at the five-fold-coordinated Ti$^{4+}$ (Ti$_{5c}$) site and its carbonyl C atom bound to a nearby bridge-bonded oxygen (O$_b$) atom, respectively. During 355 nm irradiation, the dioxymethylene intermediate can transfer an H atom to the O$_b$ atom, thus forming HCOO$^-$ directly, which is considered as the main reaction channel. In addition, the dioxymethylene intermediate can also transfer methylene to the C$_b$ row and break the C–O bond, thus leaving the original carbonyl O atom at the Ti$_{5c}$ site. After the transfer of methylene, several pathways to products are available. Thus, we have found that O$_b$ atoms are intimately involved in the photoinduced decomposition of CH$_2$O on the rutile TiO$_2$(100)-(1×1) surface.

Key words: Rutile TiO$_2$(100)-(1×1), Formaldehyde, Temperature-programmed desorption, Photoinduced decomposition

I. INTRODUCTION

Titanium dioxide (TiO$_2$), is one of the most important metal oxides used in catalysis and photocatalysis [1–5]. Formaldehyde (CH$_2$O) is a key species (reagent, intermediate, or product) in various catalytic and photocatalytic reactions, such as methanol (CH$_3$OH) synthesis [6–8], CH$_3$OH oxidation [9–13], and hydrocarbon production [14, 15]. In addition, CH$_2$O is one of the main indoor air pollutants in our daily life. It has been reported that TiO$_2$-based catalysts are widely used in thermally catalytic and photocatalytic reactions involving CH$_2$O. Therefore, it is of significant importance to gain an insightful understanding of the interactions of CH$_2$O with TiO$_2$ surfaces.

The adsorption and reactions of CH$_2$O on TiO$_2$ surfaces have been extensively studied both experimentally and theoretically [16–29]. It has been well-established that CH$_2$O can adsorb on TiO$_2$ surfaces in two different configurations [19, 21–23, 25, 28, 29]. First, CH$_2$O can weakly adsorb at a surface 5-fold-coordinated Ti$^{4+}$ (Ti$_{5c}$) site in a monodentate configuration ($\eta^1$-CH$_2$O), where it binds weakly via its O atom to the surface Ti$_{5c}$ atom. Alternatively, it can also adsorb in a bidentate fashion ($\eta^2$-CH$_2$O), where it binds to the surface strongly with its O atom bound to a surface Ti$_{5c}$ atom, and its C atom bound to an adjacent bridging oxygen (O$_b$) atom. When TiO$_2$ surfaces contain bridging oxygen vacancy (O$_v$) sites, CH$_2$O can adsorb at O$_v$ sites [20, 23, 29]. Further heating may result in the formation of other products via the carbon-carbon coupling reactions of two CH$_2$O molecules, such as ethylene (C$_2$H$_4$) [19, 21–23, 29]. In addition, the possibility of forming paraformaldehyde chains on rutile TiO$_2$(110) has also been reported by Will and coworkers [25, 30].

The photochemistry of CH$_2$O has also been investigated extensively on various TiO$_2$ surfaces and formate (HCOO$^-$) is observed as a main product [17–19, 27, 29, 31]. On rutile TiO$_2$(110), Xu and coworkers found that the photoinduced decomposition of CH$_2$O could occur efficiently to produce HCOO$^-$, methyl radical (CH$_3$), and C$_2$H$_4$ in the absence of surface oxygen species [17]. It was proposed that although lattice oxygen atoms may not appear in HCOO$^-$ product, they are intimately involved in the photoinduced decomposition of CH$_2$O on rutile TiO$_2$(110). Later, Cremer and coworkers reported that the formation of HCOO$^-$ is the dominant reaction channel and the efficiency of HCOO$^-$. 

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formation on rutile TiO$_2$(110) with surface oxygen species is about 4 times larger than that without surface oxygen species [18]. On the reduced anatase TiO$_2$(001)- (1×4) [27] and rutile TiO$_2$(011)- (2×1) surfaces [29], the photolysis of CH$_2$O also produces HCOO$^-$ as the main product in the absence of surface oxygen species. The rutile TiO$_2$(100)-(1×1) surface is one of the common facets of rutile TiO$_2$, but the photochemistry of CH$_2$O on the rutile TiO$_2$(100)-(1×1) surface has not been reported and an insightful understanding of photocatalytic reactions of CH$_2$O on the rutile TiO$_2$(100)-(1×1) surface is thus lacking. In this work, we have investigated the photocatalytic reactions of CH$_2$O on the rutile TiO$_2$(100)-(1×1) surface at 355 nm with temperature-programmed desorption (TPD) method. Without irradiation, nearly no thermal reaction products are observed. Under UV irradiation, CH$_2$O is mainly decomposed into HCOO$^-$. While, CH$_3$OH, CH$_4$, and C$_2$H$_4$ are detected as minor products at elevated temperature during the TPD process. These results will help broaden the fundamental understandings of CH$_2$O photochemistry on TiO$_2$ surfaces.

II. EXPERIMENTAL METHODS

TPD experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure of 6×10$^{-11}$ Torr. Details of this TPD apparatus have been described elsewhere [10]. TPD signals were detected by a quadrupole mass spectrometer (Extrel). The third harmonic (355 nm) output of a diode pumped, solid state, Q-switched 1064 nm laser (Spectra-Physics) was used as the UV light resource for the photocatalytic reactions of CH$_2$O in our experiments. The laser was operated with a pulse time of 12 ns and a repetition rate of 50 kHz. The average power of the light used in our experiments was approximately 20 mW, corresponding to ~6.5×10$^{16}$ photons/(cm$^2$-s).

The rutile TiO$_2$(100) single crystal was purchased from Princeton Scientific Corp., with a size of 10 mm×10 mm×1 mm. The surface was cleaned by repeated cycles of Ar$^+$ sputtering and annealing in >4×10$^{-7}$ Torr O$_2$ at 800 K. Then the ordering and cleanness of the sample were confirmed by a sharp (1×1) low energy electron diffusion (LEED) pattern and Auger electron spectroscopy (AES), respectively. CH$_2$O was obtained via the thermal decomposition of paraformaldehyde (95% purity, Sigma-Aldrich). Prior to experiments, the purity of CH$_2$O was checked by our spectrometer. The purified CH$_2$O was introduced into the surface through a calibrated molecular beam doser at about 120 K. TPD spectra were measured with a ramping rate of 2 K/s, and with the surface facing the mass spectrometer.

FIG. 1 The LEED (low energy electron diffraction) pattern for the rutile TiO$_2$(100)-(1×1) surface at $E_{\text{le}}$=50 eV after the surface cleaning process was accomplished.

III. RESULTS

A. The adsorption and reactions of CH$_2$O on the rutile TiO$_2$(100)-(1×1) surface

Before TPD experiments, the surface condition was checked by LEED and water (H$_2$O) TPD spectra, respectively. As shown in FIG. 1, a sharp (1×1) LEED pattern for the rutile TiO$_2$(100)-(1×1) surface is observed, which confirms the ordering of the surface. To further confirm the surface condition, TPD spectra of H$_2$O at different coverages were subsequently collected. At the highest H$_2$O coverage (4 ML, 1 ML=7.36×10$^{14}$ molecules/cm$^2$), four main desorption features at 147, 167, 242, and 300 K are detected in our TPD spectra (FIG. 2), which is similar to previous results of H$_2$O on the rutile TiO$_2$(100)-(1×1) surface [32, 33], indicating that a well-defined and unreconstructed (1×1) surface has been obtained. On the basis of previous studies [32, 33], the 147, 167, 242, and 300 K peaks are due to desorption of H$_2$O from multilayer (ice layer), second layer, molecular adsorption at Ti$_{5c}$ sites, and dissociative adsorption at Ti$_{5c}$ sites, respectively. Whereas, no desorption peak at higher temperature is detected, implying that no surface O$_x$ sites exist on the surface.

Afterwards, we carried out experiments with CH$_2$O adsorption on the rutile TiO$_2$(100)-(1×1) surface. As shown in FIG. 3, TPD spectra were collected at a mass-to-charge ratio (m/z) of 30 (CH$_2$O$^+$) after rutile TiO$_2$(100)-(1×1) surfaces were dosed with different coverages of CH$_2$O. At low coverages (<0.26 ML), a single desorption peak appears at ~310 K and increases in intensity with increasing CH$_2$O coverage, and its peak position nearly keeps unchanged. When the CH$_2$O coverage is higher than 0.26 ML, an additional desorption peak appears at around 260 K. As CH$_2$O coverage increases, the intensity of the 260 K peak increases, with its peak position shifting to lower temperature until 255 K. Although the 310 K peak is seriously overlapped
FIG. 2 Typical spectra collected at mass-to-charge \((m/z)\) of 18 (H\(_2\)O\(^+\)) after the rutile TiO\(_2\)(100)-(1\(\times\)1) surfaces were dosed with various coverages of H\(_2\)O at 120 K.

FIG. 3 Typical spectra collected at mass-to-charge \((m/z)\) of 30 (CH\(_2\)O\(^+\)) after the rutile TiO\(_2\)(100)-(1\(\times\)1) surfaces were dosed with various coverages of CH\(_2\)O at 120 K.

FIG. 4 The rutile TiO\(_2\)(100)-(1\(\times\)1) surfaces were dosed with 0.52 ML of CH\(_2\)O at 120 K. Typical TPD spectra collected at \(m/z = 15\) (CH\(_3\)\(^+\)), 18 (H\(_2\)O\(^+\)), 27 (C\(_2\)H\(_4\)\(^+\)), 28 (C\(_2\)H\(_4\)\(^+\), CO\(^+\)), 29 (HCO\(^+\)), 30 (CH\(_3\)O\(^+\)), 31(CH\(_3\)OH\(^+\)), 32 (CH\(_3\)OH\(^+\)), and 46 (HCOOH\(^+\)) following 0 min (red lines) and 20 min (blue lines) irradiation.

with the 260 K peak, the occurrence of two desorption peaks shows the possibility of two different CH\(_2\)O adsorption configurations on the rutile TiO\(_2\)(100)-(1\(\times\)1) surface. Since the lowest surface temperature that we could achieve in this work is 120 K, the highest coverage of CH\(_2\)O on the rutile TiO\(_2\)(100)-(1\(\times\)1) surface is about 0.75 ML.

Based on previous TPD results of CH\(_2\)O on rutile TiO\(_2\)(110) [17], the desorption of \(\eta^1\)-CH\(_2\)O gives a TPD peak at 280 K. Theoretical calculations [19, 20, 23-25] predict that the \(\eta^1\) configuration of CH\(_2\)O has an adsorption energy of ~0.7 eV, and the \(\eta^2\) configuration has an adsorption energy of ~1.3 eV. CH\(_2\)O may also adsorb at O\(_5\) sites with an adsorption energy of about 0.89–0.99 eV. Thus, \(\eta^2\)-CH\(_2\)O is the more stable adsorption configuration. However, only the \(\eta^1\) configuration of CH\(_2\)O can be formed on rutile TiO\(_2\)(110) after adsorption, and the transition from the \(\eta^1\) configuration to the \(\eta^2\) configuration requires a long time [23]. In this work, the rutile TiO\(_2\)(100)-(1\(\times\)1) surface contains no O\(_5\) sites, and thus CH\(_2\)O can only adsorb at Ti\(_{5c}\) sites. As shown in the CH\(_2\)O TPD spectra (FIG. 3), the peak position of the 310 K peak is only about 55 K higher than that of the 255 K peak. According to the first-order thermal desorption model (with a typical pre-exponential factor value of 10\(^{13}\)/s) [34], the difference between desorption energies of these two peaks is less than 0.2 eV. Therefore, the 310 and 255 K peaks could not be due to desorption of \(\eta^2\)-CH\(_2\)O and \(\eta^1\)-CH\(_2\)O, respectively. Conversely, the two desorption peaks may be due to desorption of \(\eta^1\)-CH\(_2\)O at Ti\(_{5c}\) sites. Because the population of Ti\(_{5c}\) sites on the rutile TiO\(_2\)(100)-(1\(\times\)1) surface is about 1.5 times bigger than that on rutile TiO\(_2\)(110), the repulsive interaction between CH\(_2\)O molecules adsorbed at Ti\(_{5c}\) sites on the rutile TiO\(_2\)(100)-(1\(\times\)1) surface will be much stronger than that on rutile TiO\(_2\)(110). In this case, the appearance of the 255 K peak is likely the result of the strong intermolecular repulsions between CH\(_2\)O molecules adsorbed at Ti\(_{5c}\) sites.

In addition to desorbed parent CH\(_2\)O, other possible desorption products were examined by comprehensively monitoring various signals of \(m/z = 15, 18, 27, 28, 29, 30, 31, 32,\) and 46 (FIG. 4). No evidence of other re-
action products was found. The phenomenon is also observed on anatase TiO$_2$(101) [28]. But it is considerably different from the phenomenon observed on rutile TiO$_2$(110) [19, 21, 22], rutile TiO$_2$(100)-(2×1) [29], and the reduced anatase TiO$_2$(100)-(1×4) surfaces [27]. On these surfaces [19, 21, 22, 27, 29], two CH$_2$O molecules can be coupled to form C$_2$H$_4$, and surface O$_h$ sites are identified as the reactive sites for the formation of C$_2$H$_4$. In our experiments, the rutile TiO$_2$(100)-(1×1) surface used is annealed in >4×10$^{-7}$ Torr O$_2$, and nearly no surface O$_h$ sites exist on the rutile TiO$_2$(100)-(1×1) surface after sample preparation. Therefore, it is reasonable that no thermal products are detected after CH$_2$O adsorption.

B. The photocatalytic reactions of CH$_2$O on the rutile TiO$_2$(100)-(1×1) surface

FIG. 5 shows TPD spectra acquired at mass-to-charge ratios (m/z) of 28 (CO$^+$, C$_2$H$_4^+$), and 30 (CH$_2$O$^+$) after rutile TiO$_2$(100)-(1×1) surfaces were dosed with 0.52 ML of CH$_2$O and then irradiated by a laser at 355 nm for various durations. Before irradiation, the signal profiles of the 260 K peak and the 310 K peak from m/z=28 are exactly same as those from m/z=30, suggesting that both peaks are the results of dissociative ionization of desorbed parent CH$_2$O molecules in the electron-bombardment ionizer. As mentioned above, no other reaction products are detected, implying that this surface is thermally inactive for the reactions of CH$_2$O.

After UV irradiation, both CH$_2$O peaks at 260 and 310 K decrease monotonically as the laser irradiation time increases, suggesting that CH$_2$O molecules are either photo-desorbed or reacted to form other products. A TPD peak at ~440 K becomes obvious in the TPD trace of m/z=30 after irradiation and keeps nearly unchanged with increasing irradiation time (FIG. 5(a)). Taking into account additional traces of m/z=29 (FIG. 4), this peak is also assigned to desorption of CH$_2$O. This result suggests that part of CH$_2$O molecules have become more strongly bound to the surface after irradiation. A similar phenomenon has been observed on rutile TiO$_2$(110) [17], which may be due to the formation of η$_2$-CH$_2$O after irradiation.

CH$_2$O$_{Ti5c}$+O$_h$→O$_h$-CH$_2$-O$_{Ti5c}$  

(1)

In our work, the 440 K peak is also likely due to the formation of η$_2$-CH$_2$O. Based on previous work of aldehydes photochemistry on rutile TiO$_2$(110) [35], the O$_{Ti5c}$-CH$_2$O$_h$ species is very photoactive, and can be easily decomposed into HCOO$^-$. As a result, the amount of η$_2$-CH$_2$O on the surface will not keep increasing with increasing irradiation time.

Concomitant to the decrease in the CH$_2$O TPD peaks, the TPD signal for m/z=28 at around 580 K increases with increasing irradiation time (FIG. 5(b)).

Considering the small adsorption energy of CO on the surface, the 580 K peak could only come from the thermal decomposition of other species. In order to determine the origin of this new feature, TPD traces were collected at a variety of m/z ratios (FIG. 4). On the basis of the TPD results in FIG. 4, the m/z=28 signal at 580 K may come from three sources. Compared with previous results of HCOOH on rutile TiO$_2$(100) [36] and the cracking patterns of HCOOH observed in our mass spectrometer, the first two sources of m/z=28 signal at 580 K are HCOOH and HCOO$^-$, both of which could be the products of CH$_2$O photo-oxidation.

The large TPD signal seen in FIG. 5(b) indicates that HCOO$^-$ may be an important photoinduced product. Compared to other products, the intensity of the 580 K peak is several times greater (see FIG. 4), strongly suggesting that HCOO$^-$ is probably the major product of the photoinduced decomposition of CH$_2$O on the rutile TiO$_2$(100)-(1×1) surface. The yields of CO (from HCOO$^-$) and CH$_2$O with increasing irradiation time are calculated and displayed in FIG. 6. About 0.19 ML of CH$_2$O is depleted after 20 min irradiation, whereas, only 0.023 ML of HCOO$^-$ is produced, implying that the decrease of the CH$_2$O signal is mainly the result of photoinduced desorption of CH$_2$O during laser irradiation.

In order to produce HCOO$^-$, the C atom of the CH$_2$O molecule must acquire a second O atom. According to previous work [17], without additional sur-

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face oxygen species, the second O atom is either from an O₂ row or from another adsorbed CH₂O molecule. The direct photodissociation of CH₂O to produce an O atom via the C=O bond cleavage is not possible because of the extremely low adsorption cross section of CH₂O at 355 nm (∼10⁻²⁰ cm²) [37]. Xu and coworkers [17] proposed that an O atom at the Ti⁵c site (O_{Ti⁵c}) can be produced via the transfer of methylene from CH₂O to an O₆ atom during UV irradiation through an intermediate adsorption structure consisting of dioxymethylene.

\[ \text{O₆-CH₂-O}_{Ti⁵c} \rightarrow \text{O₆-CH₂+O}_{Ti⁵c} \]  

(2)

Subsequently, the O_{Ti⁵c} atom may react with a nearby adsorbed CH₂O molecule to form an O_{Ti⁵c}-CH₂-O_{Ti⁵c} complex by heat or laser irradiation.

\[ \text{O}_{Ti⁵c}+\text{CH₂O}_{Ti⁵c} \rightarrow \text{O}_{Ti⁵c}-\text{CH₂-O}_{Ti⁵c} \]  

(3)

Then the complex perhaps gives rise to HCOO⁻ either by transferring an H atom to an O₆ atom (HO₆), or ejecting an H atom to the vacuum.

\[ \text{O}_{Ti⁵c}+\text{CH₂O}_{Ti⁵c}+\text{O₆} \rightarrow \text{HCOO}_{Ti⁵c}^-+\text{H}_2\text{O} \]  

(4)

\[ \text{O}_{Ti⁵c}+\text{CH₂O}_{Ti⁵c} \rightarrow \text{HCOO}_{Ti⁵c}^-+\text{H} \]  

(5)

In addition, HCOO⁻_{Ti⁵c} may combine with HO₆ to produce HCOOH.

\[ \text{HCOO}^-_{Ti⁵c}+\text{HO₆} \rightarrow \text{HCOOH}+\text{O₆} \]  

(6)

While, as shown in TPD trace of m/z=18 (FIG. 4), two main desorption features at 478 and 580 K are observed after irradiating the 0.52 ML CH₂O covered rutile TiO₂(100)-(1×1) surface for 20 min. The 580 K peak may come from thermal decomposition of HCOOH and HCOO⁻ [36]. For the 478 K peak, no signals of higher m/z ratios are detected at this temperature. Thus, this peak can be only due to the H₂O desorption. However, the desorption temperature is much higher than that of H₂O adsorbed at the Ti₅c sites of rutile TiO₂(100)-(1×1), and is similar to that of the recombinative desorption of H₂O from hydroxyls on O₆ rows of rutile TiO₂(110) [38]. Thus, the 478 K peak is also likely from recombinative desorption of H₂O.

\[ 2\text{HO₆} \rightarrow \text{H}_2\text{O}+\text{O}_2 \]  

(7)

The formation of H₂O via the reaction (7) verifies that the reaction channel involving a dioxymethylene intermediate is very possible to proceed on the surface, resulting in the formation of HCOO⁻ eventually.

The reaction channel consisting of a dioxymethylene intermediate is also supported by the observation of other products. As shown in FIG. 7(a), typical TPD spectra of m/z=27 (C₂H₅⁺) were collected after irradiating the 0.52 ML CH₂O covered rutile TiO₂(100)-(1×1) surfaces for different time with a laser at 355 nm. Before irradiation, no signal is observed. As irradiation time increases, a peak at ∼580 K appears and increases in intensity. Based on previous works [17, 19, 21, 22], this peak is due to desorption of C₂H₄ product, which is formed via the carbon-carbon coupling of two CH₂O molecules. Clearly, C₂H₄ product is another source for the m/z=28 signal at 580 K. This is very similar to the observation of CH₂O photodecomposition on the rutile TiO₂(110) surface. On rutile TiO₂(110), the C₂H₄ product arises from CH₂O adsorbed at O₆ sites to form a diolate (-OCH₂CH₂O-) species, which releases C₂H₄ at a relatively high temperature [21, 22]. But the rutile TiO₂(100)-(1×1) surface used in our work contains no O₆ sites. Thus, the dioxymethylene species may act as the intermediate for the formation of C₂H₄. After the transfer of methylene to O₆ atoms, two O₆-CH₂ groups may be coupled to form C₂H₄.

\[ 2\text{O₆-CH₂} \rightarrow \text{C₂H₄+2O₆} \]  

(8)

While, another desorption peak appears at 570 K in the TPD spectrum of m/z=15 (C₃H₆⁺) after UV irradiation and increases with irradiation time (FIG. 7(b)). This peak is attributed to CH₃ radical desorption, probably from O₆ atoms. The formation of CH₃O₆ may also need the participation of O₆-CH₂ groups.

\[ \text{O₆-CH₂+HO₆} \rightarrow \text{O₆-CH₃+O₆} \]  

(9)

\[ \text{O₆-CH₃} \rightarrow \text{CH₄+O₆} \]  

(10)

The appearance and increase of CH₃ on O₆ atoms further demonstrate that methylene groups can be transferred to O₆ atoms during irradiation. Therefore, it can be concluded that the reaction channel involving the dioxymethylene intermediate is very likely to proceed on the rutile TiO₂(100)-(1×1) surface. It is also noteworthy that the intensity of CO signal at 580 K is about 20 times bigger than that of C₂H₄ signal, and about 40 times bigger than that of CH₃ signal after 20 min irradiation (see FIG. 5 and FIG. 7).
These results suggest that the dominant photocatalytic reaction is the formation of HCOO$^-$. Meanwhile, at the first 1 min irradiation, nearly no $C_2H_4$ and $CH_3$ products are formed (FIG. 7), but the HCOO$^-$ product has been largely formed (bigger CO desorption signal in FIG. 5(b)). In other words, the formations of $C_2H_4$ and $CH_3$ are not exactly coincident with the formation of HCOO$^-$. The formation of HCOO$^-$ precedes the formations of $C_2H_4$ and $CH_3$. As a result, the formation of HCOO$^-$ may not completely depend on the formation of the $O_{Ti5c}$ atoms. On the contrary, the $O_b$-$CH_2$-$O_{Ti5c}$ intermediate is likely to decompose into HCOO$^-$directly, transferring an H atom to the nearby $O_b$ atom ($HO_b$).

$$O_b$-$CH_2$-$O_{Ti5c}$+$O_b$$\rightarrow$$HCOO_b$-$O_{Ti5c}$-$^-$$+$$HO_b$$ \quad (11)$$

In addition to the increase in the $m/z=28$ signal at around 580 K, a new desorption peak appears at about 570 K in the TPD trace of $m/z=31$ (FIG. 8) and increases with increasing irradiation time. Taking into account additional TPD traces in FIG. 4, this peak is attributed to desorption of CH$_3$OH. This phenomenon has been observed previously on rutile TiO$_2$(110) [19] and the reduced anatase TiO$_2$(100)-(1×4) surface [27]. In Huang’s experiment [19], they proposed that the occurrence of H-transfer between HCOO$^-$ and dioxymethylene led to the formation of methoxy species (CH$_3$O). The disproportionation reaction between CH$_3$O could lead to the formation of CH$_3$OH and CH$_2$O at elevated temperature. Previous results of CH$_3$O on rutile TiO$_2$(001) also show that the coincident desorption of CH$_3$OH and CH$_2$O could occur at 370 and 550 K, respectively [16]. However, we did not observe the coincident desorption of CH$_3$OH and CH$_2$O at 570 K. Based on previous work on rutile TiO$_2$(110) [39], CH$_2$O can recombine with $HO_b$ to form CH$_3$OH again. On the reduced anatase TiO$_2$(100)-(1×4) surface [27], Wang and coworkers also ascribed the formation of CH$_3$OH to the reaction of CH$_2$O with the produced H atoms during irradiation or during the heating process. Thus, on the rutile TiO$_2$(100)-(1×1) surface, the formation of CH$_3$OH may proceed as follows:

$$CH_2O_{Ti5c}+HO_b$$\rightarrow$$O_{Ti5c}$-$CH_3$+$O_b$$ \quad (12)$$

$$O_{Ti5c}$-$CH_3$+$HO_b$$\rightarrow$$CH_3OH$$ \quad (13)$$

While, during the TPD process, $CH_3O_{Ti5c}$ may also decompose into $CH_3$ and $O_{Ti5c}$.

$$O_{Ti5c}$-$CH_3$$\rightarrow$$CH_3$-$^+$+$O_{Ti5c}$$ \quad (14)$$

**IV. DISCUSSION**

Although CH$_3$O is a very simple molecule, the photoysis of this molecule is very complicated. The products and reaction channels for CH$_3$O decomposition on different TiO$_2$ surfaces [19, 21, 22, 27, 29] are very similar. For rutile TiO$_2$(100)-(1×1) and anatase TiO$_2$(101) surfaces [28], however, no other thermal reaction products were detected during the TPD process due to the absence of $O_b$ sites on the surfaces. This result is also an evidence that $O_b$ sites are the reactive sites for the carbon-carbon coupling of CH$_3$O to C$_2$H$_4$. Among all these TiO$_2$ surfaces discussed above, the desorption temperature of CH$_3$O is the highest on the rutile
TiO2(100)-(1×1) surface. That may be due to the fact that the densities of Ti5c and O6h atoms on the rutile TiO2(100)-(1×1) surface are much higher than those on the other TiO2 surfaces. As a result, the carbonyl C atom of the CH2O molecule may interact with the O6h atom more easily, which may result in the formation of a more stable adsorption configuration.

The rutile TiO2(100)-(1×1) surface is thermally inactive for the reactions of CH3O, but it is photoactive for the reactions of CH2O. The main decomposition product is HCOO−, which is similar to the results obtained on other TiO2 surfaces [17, 19, 27, 29]. However, the dominant reaction channels leading to HCOO− formation may be different. On the rutile TiO2(110) surface, the dominant reaction channel is consisted of the O5c atoms formation via the transfer of methylene to the O6h sites and the O6h-CH2-O5c species acts as the intermediate [17]. Whereas, on the rutile TiO2(100)-(1×1) surface, the case is very different. As shown in Fig. 5 and Fig. 7, the intensity of CO signal at 580 K is about 20 times bigger than that of C2H4 signal, and about 40 times bigger than that of CH3 signal. These values are much bigger than the ratios of those produced from CH2O photodecomposition on rutile TiO2(110) [17]. As mentioned above, the formations of C2H4 and CH3 require the transfer of methylene to the O6h sites forming O6hCH2. After the transfer process, the O5c atoms are produced simultaneously, which will take part in the following formation of HCOO−. Whereas, the formation of HCOO− precedes the formation of C2H4 and CH3 in this work. These results clearly indicate that O5c is probably not necessary for the formation of HCOO−. Therefore, the dominant reaction channel on the rutile TiO2(100)-(1×1) surface may be changed. The direct decomposition of O6h-CH2-O5c into HCOO−O5c+ and OH6h becomes the main reaction channel, while the reaction of O5c with CH2O adsorbed at Ti5c sites to produce HCOO− becomes a minor reaction channel. Therefore, on the rutile TiO2(100)-(1×1) surface, two possible reaction channels may lead to the formation of HCOO− and the O6h-CH2-O5c species maybe acts as the intermediate. The direct decomposition is considered as the dominant reaction channel and the lattice oxygen atom (O6h) is directly involved in the photodecomposed decomposition of CH2O on the rutile TiO2(100)-(1×1) surface.

V. CONCLUSION

In this work, we have investigated the interactions of CH2O with a rutile TiO2(100)-(1×1) surface under UV irradiation. Experimental results show that the photodecomposition of CH2O on the rutile TiO2(100)-(1×1) surface can occur easily under UV light irradiation. Before irradiation, only molecular desorption of CH2O can be detected during the TPD process. When irradiated by UV light, several photodecomposed products are detected. HCOO− is the major product, while C2H4, CH3, and CH3OH are minor products.

Our TPD investigation demonstrates that O6h atoms play a very important role in the photodecomposed decomposition of CH2O on the rutile TiO2(100)-(1×1) surface through an initial O6h-CH2-O5c intermediate structure. Clear mechanisms have been delineated for the participation of lattice (O6h) atoms in the decomposition pathways, including their presence in one type of HCOO− product. Our results are supposed to broaden the fundamental understanding of CH2O photochemistry on TiO2 surfaces.

VI. ACKNOWLEDGMENTS

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