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Photocatalytic Cross-Coupling of Methanol and Formaldehyde on a Rutile TiO_2(110) Surface

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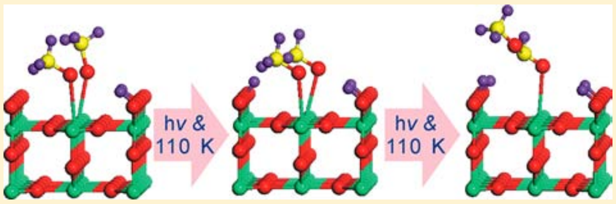
ABSTRACT: The photocatalytic oxidation of methanol on a rutile TiO_2(110) surface was studied by means of thermal desorption spectroscopy (TDS) and X-ray photoelectron spectroscopy (XPS). The combined TDS and XPS results unambiguously identify methyl formate as the product in addition to formaldehyde. By monitoring the evolution of various surface species during the photocatalytic oxidation of methanol on TiO_2(110), XPS results give direct spectroscopic evidence for the formation of methyl formate as the product of photocatalytic cross-coupling of chemisorbed formaldehyde with chemisorbed methoxy species and clearly demonstrate that the photocatalytic dissociation of chemisorbed methanol to methoxy species occurs and contributes to the photocatalytic oxidation of methanol. These results not only greatly broaden and deepen the fundamental understanding of photochemistry of methanol on the TiO_2 surface but also demonstrate a novel green and benign photocatalytic route for the synthesis of esters directly from alcohols or from alcohols and aldehydes.



1. INTRODUCTION

Photocatalysis has received remarkable interest as a green and sustainable solution for energy and environmental issues since Fujishima and Honda's first reports of UV-light-induced redox chemistry on TiO_2.[1] Among various photocatalytic reactions, the photocatalytic conversion of methanol is of particular importance. Methanol as a hole scavenger greatly enhances the activity of photocatalysts in photocatalytic splitting of water to hydrogen.[2] The photocatalysis of methanol is also prominent in environmental photocatalysis,[3] photocatalytic selective oxidation,[4] and photocatalytic reforming reactions.[5] Meanwhile, as a simple prototype for many organic compounds, methanol is adopted as the probe molecule for the fundamental studies of complex photocatalytic reactions on oxide surfaces.

Many experimental and theoretical studies have been performed to study the chemistry and photochemistry of methanol on the rutile TiO_2(110) surface, a typical model catalyst of TiO_2.[6−10] Methanol dissociates primarily on oxygen vacancies and steps of TiO_2(110) surface; on the ideal TiO_2(110) surface methanol molecularly chemisorbs, but arguments still exist on whether methanol can dissociate on the Ti^{4+} sites.[11−26] Recently, the photochemistry of methanol on the TiO_2(110) surface has been explored.[24,27−32] Methanol can be photocatalyzed into formaldehyde, and chemisorbed methoxy species was identified to be the active species. Henderson et al. proposed that chemisorbed methoxy species is formed only by the thermal dissociation of methanol on TiO_2(110).[27,30,31] Yang et al. proposed that molecularly chemisorbed methanol on Ti^{4+} sites of TiO_2(110) can undergo the photocatalytic dissociation to form chemisorbed methoxy species.[24,29,32] However, by far, only formaldehyde has been observed as the product of methanol photocatalytic oxidation on TiO_2(110) surface, which is in dramatic contrast to the rich photochemistry of methanol on TiO_2-based catalysts. Meanwhile, only very few spectroscopic studies have been reported on the photochemistry of methanol on rutile TiO_2(110) surface.[33,34]

In a recent work, Phillips et al.[35] first reported the sequential photooxidation of methanol to methyl formate on TiO_2(110) covered with O adatoms by means of thermal desorption spectroscopy (TDS), scanning tunneling microscopy (STM), and theoretical calculations. Very recently, Guo et al.[36] also reported the formation of methyl formate as the product of photooxidation of methanol on bare TiO_2(110) by means of TDS. Here, we report our combined TDS and X-ray photoelectron spectroscopy (XPS) study of methanol photocatalytic oxidation on the bare TiO_2(110) surface in which methyl formate was observed as the product in addition to formaldehyde. By monitoring the evolution of various surface species during the photocatalytic oxidation of methanol on the TiO_2(110) surface, our XPS results for the first time give direct spectroscopic evidence for the formation of methyl formate as the product of photocatalytic cross-coupling of chemisorbed formaldehyde with chemisorbed methoxy species and clearly demonstrate that the photocatalytic dissociation of chemisorbed methanol to methoxy species occurs and contributes to the photocatalytic oxidation of methanol.

2. EXPERIMENTAL SECTION

All experiments were performed in a Leybold stainless-steel ultrahigh vacuum (UHV) chamber with a base pressure of 1.2×10^{-10} mbar. The UHV chamber was equipped with facilities for X-ray photoelectron spectroscopy with the newly installed XR 50 X-ray source

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(SPECS GmbH) and PHBIOS 100 MCD hemispherical energy analyzer (SPECS GmbH), ultraviolet photoelectron spectroscopy, low energy electron diffraction, and differential-pumped thermal desorption spectroscopy. The rutile $TiO_2(110)$ single crystal purchased from MaTeck was mounted onto a Ta support plate (1 mm thick and of the same dimensions as the crystal) with a high temperature alumina-based inorganic adhesive (Aremco 503) and graphite powder (99.9995%, Alfa Aesar China Co., Ltd.). The Ta support was cooled and resistively heated by two Ta wires spot-welded to its back side. The sample temperature could be controlled between 100 and 1273 K and was measured by a chromel-alumel thermocouple spot-welded to the backside of the sample. Prior to experiments, the $TiO_2(110)$ sample was cleaned by repeated cycles of Ar ion sputtering and annealing at 1000 K for 10 min until LEED gave a sharp (1×1) diffraction pattern and no contaminants could be detected by XPS.

Methanol (99.8%, Sinopharm Chemical) was purified by repeated freeze−pump−thaw cycles. Formaldehyde was generated via thermal decomposition of paraformaldehyde (95%, Sinopharm Chemical) in a glass tube connected to the UHV apparatus. Prior to experiments, paraformaldehyde was thoroughly degassed by overnight pumping at 60 °C. The purity of all reactants was checked by QMS prior to experiments. A line-of-sight stainless steel doser (diameter: 8 mm) positioned ∼2 cm in front of the $TiO_2(110)$ surface was used for the exposures of methanol and formaldehyde to keep the chamber pressure below 5×10^{-10} Torr. The doser could be retracted 50 mm after the exposure. All exposures were reported in Langmuir ($1\ L = 1.0 \times 10^{-6}$ Torr·s) without corrections for the gauge sensitivity. During the TDS measurements, the sample was positioned ∼1 mm away from a collecting tube of a differential-pumped QMS, and the heating rate was 2 K/s. XPS spectra were recorded using Mg Kα radiation ($h\nu$ = 1253.6 eV) with a pass energy of 20 eV. The C 1s XPS spectrum was peak-fitted with the XPSPEAK software (Version 4.1), and the line shape (%Gaussian − Lorentzian = 80%) and full-width at half-maximum (1.50 eV) were fixed during the peak-fitting process.

The UV irradiation was accomplished using a 100 W high-pressure Hg arc lamp (Oriel 6281), which provides a pressure-broadened emission spectrum from gaseous Hg in the UV-light region. When the light wavelength is below 250 nm, the light irradiance of this source decreases rapidly and is only 0.05 mW/m^2 for the 200 nm light at a distance of 0.5 m.[37] The absorption of methanol in the UV region below 200 nm can thus be neglected under our experimental condition. A water filter was used to remove the IR portion of the emission spectrum. The UV-light was focused onto the tip of a single strand, 0.6 mm diameter fused silica fiber optic cable that directed the light through a UHV-compatible feedthrough onto the $TiO_2(110)$ face without exposure to extraneous surfaces. Exposure of $TiO_2(110)$ crystal at 110 K to the UV-light resulted in the rising of crystal temperature no more than 3 K.

3. RESULTS AND DISCUSSION

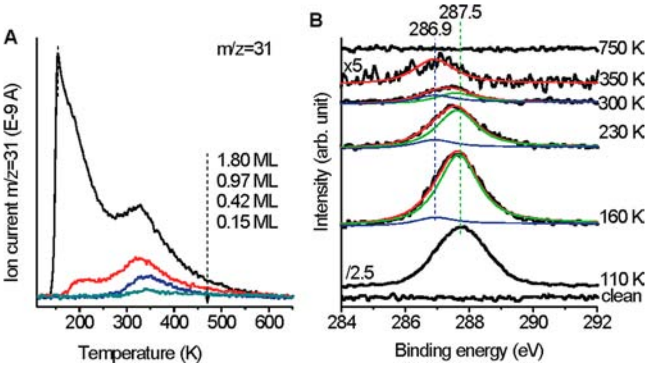

Figure 1. (A) TDS spectra of m/z = 31 (methanol) after the $TiO_2(110)$ surface was exposed to 0.15, 0.42, 0.97, and 1.80 ML methanol at 110 K. (B) C 1s XPS spectra after the $TiO_2(110)$ surface was exposed 1.80 ML methanol at 110 K and flashed to the indicated temperatures.

Figure 1A shows CH_3OH TDS spectra from $TiO_2(110)$ surfaces covered with 1.80, 0.97, 0.42, and 0.15 ML (1 ML = 5.2×10^{14} sites·cm^{-2}) adsorbed methanol that could be reproducibly prepared by a 0.014 L CH_3OH exposure at 110 K, a 0.014 L CH_3OH exposure at 110 K, followed by the flash to 160, 230, and 300 K, respectively. Agreeing with previous results,[15−18] four CH_3OH desorption features were observed at ∼154, ∼210, ∼330, and ∼495 K, respectively corresponding to the molecular desorption of physisorbed CH_3OH, $CH_3OH(a)$ chemisorbed on the bridging-bonded O sites, $CH_3OH(a)$ chemisorbed on the Ti^{4+} sites, and the recombinative desorption of methoxy species ($CH_3O(a)$). The saturating coverage of $CH_3OH(a)$ chemisorbed on the Ti^{4+} sites was herein defined as 0.77 ML.[15,26] Figure 1B shows C 1s XPS spectra after the $TiO_2(110)$ surface covered with 1.80 ML adsorbed methanol was flashed to elevated temperatures. The $TiO_2(110)$ surface covered with 1.80 ML adsorbed methanol gives an intense and broad C 1s peak with the binding energy at 287.5 eV, corresponding to adsorbed $CH_3OH(a)$.[18] Flashing the surface to elevated temperatures desorbs adsorbed $CH_3OH(a)$ from the surface and results in the weakening of C 1s XPS feature at 287.5 eV; meanwhile, the existence of additional C 1s feature becomes evident. For example, the C 1s XPS spectrum of the surface flashed to 300 K is broadened and asymmetric, and that of the surface flashed to 350 K exhibits a weak peak centering at 286.9 eV. Thus, we performed the peak-fitting analysis of the C 1s XPS spectra of surfaces flashed to elevated temperatures and found that these C 1s XPS spectra could be well fitted with two components with binding energies at 287.5 and 286.9 eV. The C 1s feature at 286.9 eV can be assigned to be $CH_3O(a)$ species on $TiO_2(110)$.[18] These XPS results agree with previous reports of the formation of methoxy species upon methanol adsorption on $TiO_2(110)$. Estimated from the integrated peak areas of C 1s features, the coverages of $CH_3OH(a)$ and $CH_3O(a)$ are, respectively, 1.73 and 0.07 ML on $TiO_2(110)$ surface exposed to 0.014 L CH_3OH at 110 K. The coverage of $CH_3OH(a)$ decreases to 0.90, 0.35, 0.08, and 0 ML after the surface was flashed to 160, 230, 300, and 350 K, respectively; correspondingly, the coverage of $CH_3O(a)$ initially does not vary, then decreases to 0.05 ML after the flash at 350 K and disappears after the flash at 750 K, corresponding to the recombinative desorption of methanol. As shown in Figure 2A, adsorbed $CH_3OH(a)$ gives the O 1s binding energy at 534.0 eV. Because of the strong interference arising from TiO_2 surface, the O 1s binding energy of chemisorbed $CH_3O(a)$

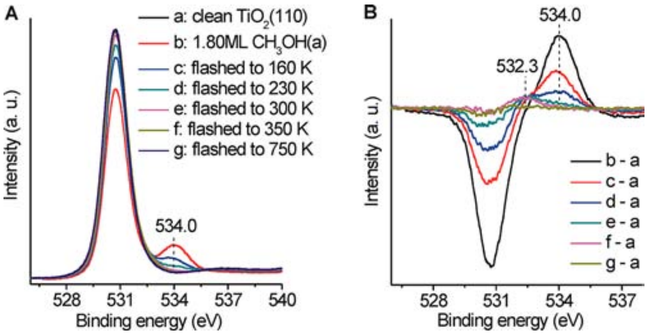

Figure 2. (A) O 1s XPS spectra after the $TiO_2(110)$ surface was exposed 1.80 ML methanol at 110 K and flashed to the indicated temperatures. (B) O 1s difference spectra obtained from (A).

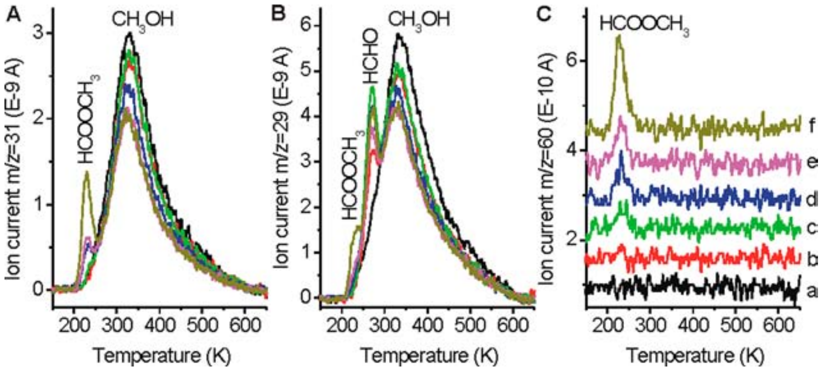

Figure 3. TDS spectra of (A) $m/z = 31$ (methanol and methyl formate), (B) $m/z = 29$ (methanol, formaldehyde, and methyl formate), and (C) $m/z = 60$ (methyl formate) after the $TiO_2(110)$ surface was exposed to 0.42 ML methanol at 110 K followed by the UV-light irradiation for 0 s (a), 30 s (b), 1 min (c), 5 min (d), 10 min (e), and 20 min (f).

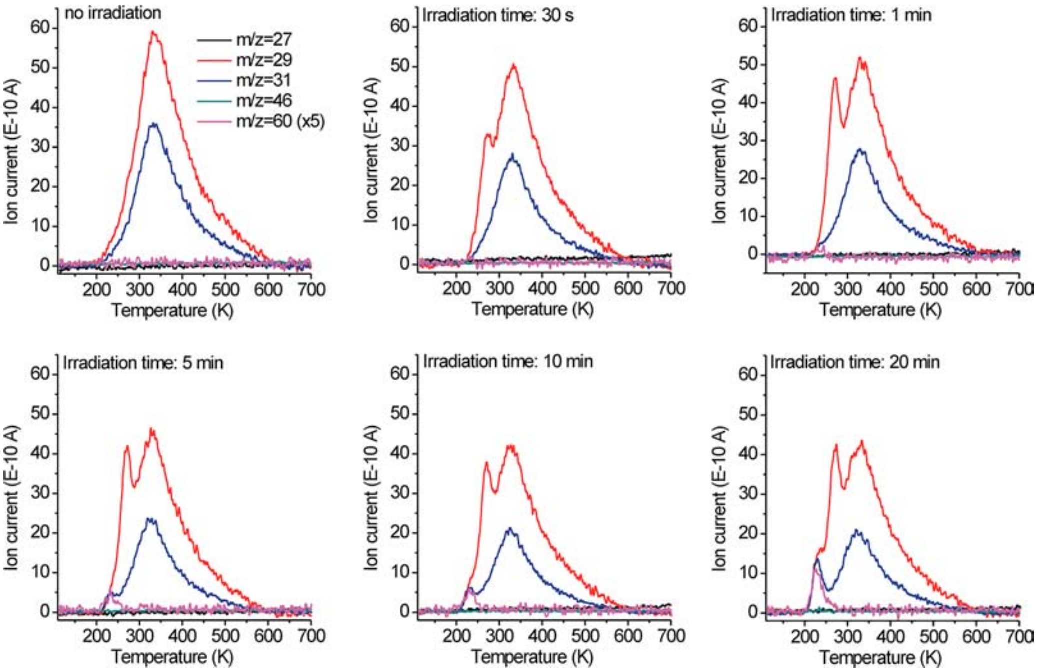

Figure 4. TDS spectra after the $TiO_2(110)$ surface was exposed to 0.42 ML methanol at 110 K followed by the UV-light irradiation for the indicated times.

species could not be unambiguously identified, but is likely located at ~532.3 eV indicated from the O 1s XPS difference spectra (Figure 2B).

Figure 3 shows TDS spectra of $m/z = 31$, 29, and 60 signals after the $TiO_2(110)$ surface covered with 0.42 ML adsorbed methanol was irradiated by the UV-light for different times. After a 30 s irradiation, the methanol desorption peak at ~330 K weakens (Figure 3A and B); meanwhile, a new desorption feature appears at ~270 K in the TDS spectrum of $m/z = 29$ signal (Figure 3B) that can be assigned to desorption of formaldehyde. This suggests the UV-light-induced photocatalytic oxidation of chemisorbed methanol to chemisorbed formaldehyde on the $TiO_2(110)$ surface, agreeing with previous reports.[27,32] With the prolonging of irradiation time, the methanol desorption peak keeps decreasing, and the formaldehyde desorption feature reaches the maximum after 1 min of irradiation but then keeps decreasing. The decrease of formaldehyde desorption feature is accompanied by the appearance and growth of a new desorption feature at ~230 K in the TDS spectra of both $m/z = 29$ and $m/z = 31$ signals. We have thus performed a careful scan of likely species by mass spectroscopy and found the desorption of the $m/z = 60$ signal that is also located at ~230 K (Figure 4). As shown in Figure 3C, the desorption feature of $m/z = 60$ signal is neglectable after 30 s of irradiation but then keeps growing with the prolonging of the irradiation time. As shown in Figure 4, the desorption features of $m/z = 60$, 31, 29 signals at ~230 K vary in the same trend under all investigated experimental conditions, demonstrating that these signals arise from the same species. Thus, the TDS results demonstrate the formation of another product as well as formaldehyde that exhibits m/z signals of 60, 31, 29 in its mass spectrum.

The photocatalytic oxidation of 0.42 ML adsorbed methanol on the $TiO_2(110)$ surface was further studied with XPS (Figure 5A). The C 1s features of chemisorbed $CH_3OH(a)$ and $CH_3O(a)$ were observed, respectively, at 287.5 and 286.9 eV on the surface prior to the irradiation. After irradiation, a new C 1s feature with the binding energy at 288.4 eV evolves. The

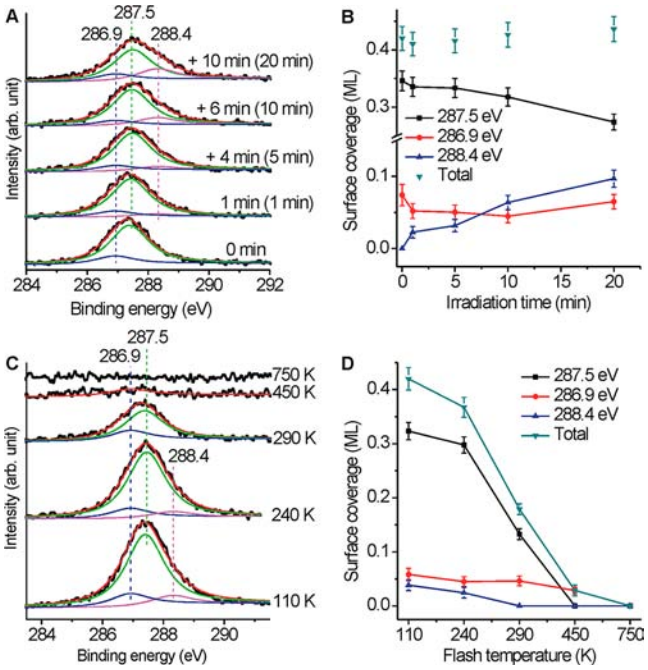

Figure 5. (A) C 1s XPS spectra and (B) the integrated C 1s peak area of each component after the $TiO_2(110)$ surface was exposed to 0.42 ML methanol at 110 K followed by the UV-light irradiation for the indicated times. Note that these data were obtained in one experiment in which the UV-light irradiation and the XPS data measurement were performed in sequences. The time in the bracket indicates the total irradiation time. (C) C 1s XPS spectra and (D) the integrated C 1s peak area of each component after the $TiO_2(110)$ surface was exposed to 0.42 ML methanol at 110 K and irradiated for 20 min followed by flashing to the indicated temperatures.

adsorption of formaldehyde on the $TiO_2(110)$ surface was comparatively studied by XPS, and the C 1s binding energy of adsorbed formaldehyde on the $TiO_2(110)$ surface was determined to be 288.5 eV (Figure 6A). Figure 5B compares the intensity variation of different C 1s features as a function of the irradiation time. With the prolonging of the irradiation time, the total intensity does not vary much, but the C 1s feature at 287.5 eV keeps weakening while that at 288.4 eV keeps growing; the C 1s feature at 286.9 eV weakens after 1 min of irradiation, then does not change much, and grows a bit after 20 min of irradiation. Figure 5C shows C 1s XPS spectra after the $TiO_2(110)$ surface covered with 0.42 ML adsorbed methanol was irradiated for 20 min and then flashed to elevated temperatures. The corresponding intensity variation of different C 1s features as a function of the flashing temperature is displayed in Figure 5D. Three C 1s features at 286.9, 287.5, and 288.4 eV are present on the surface subjected to a 20 min's irradiation. After flashing to 240 K, the features at 286.9 and 288.4 eV weaken simultaneously, corresponding to the desorption peak of m/z = 60, 31, and 29 signals at ∼230 K in the TDS spectra; further flashing to 290 K results in the disappearance of the feature at 288.4 eV and the weakening of the feature at 287.5 eV, corresponding to the desorption peak of formaldehyde at ∼270 K and the partial desorption of chemisorbed $CH_3OH(a)$, respectively; the feature at 287.5 eV disappears and the feature at 286.9 eV weakens after the flash at 450 K and the surface restores to the clean one after flashing to 750 K, corresponding to the desorption of chemisorbed $CH_3OH(a)$ and the recombinative desorption of chemisorbed $CH_3O(a)$. It could be seen that the coverages of various surface species estimated from XPS measurement of the $TiO_2(110)$ surface covered with 0.42 ML adsorbed methanol directly irradiated for 20 min (Figure 5D) differ from those estimated from XPS measurement of the same starting surface with the same total irradiation time whose irradiation and subsequent XPS measurement were divided into four sequences (the last data in Figure 5B). This indicates that the efficiency of photocatalytic reaction should be sensitive to the employed experimental procedure.

The above TDS and XPS results clearly demonstrate that, in addition to previously reported formaldehyde, a new product is formed during the photocatalytic oxidation of methanol on the $TiO_2(110)$ surface under our investigated conditions. This product gives m/z = 60, 31, 29 signals in the mass spectroscopy and gives two C 1s features with the binding energy at 286.9 and 288.4 eV in the XPS spectrum. We thus identified the product to be methyl formate ($HCOOCH_3$). Kominami et al. observed the selective oxidation of methanol to methyl formate over powder TiO_2 photocatalysts irradiated by UV-light and heated at elevated temperatures,[38] and our results clearly demonstrate the formation of methyl formation during the photocatalytic oxidation of methanol on $TiO_2(110)$ surface under UHV conditions. Chemisorbed formaldehyde formed by the photocatalytic oxidation of methanol on $TiO_2(110)$ surface participates in the reaction forming methyl formate, and likely surface reactions include (i) the thermally activated cross-coupling of formaldehyde and methanol as reported on Au surfaces,[39] (ii) the photocatalytic cross-coupling of form-

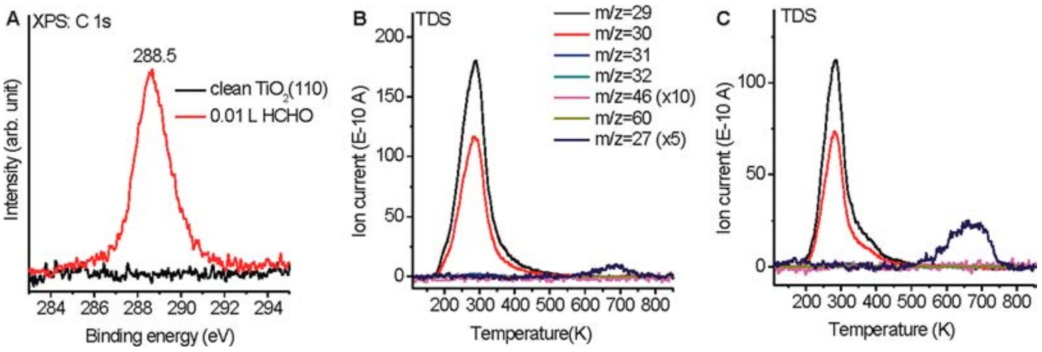

Figure 6. (A) C 1s XPS spectra after the $TiO_2(110)$ surface was exposed to 0.01 L HCHO at 110 K. (B) TDS spectra after the $TiO_2(110)$ surface was exposed to 0.01 L HCHO at 110 K. (C) TDS spectra after the $TiO_2(110)$ surface was exposed to 0.01 L HCHO at 110 K followed by a UV-light irradiation for 20 min.

aldehyde and methanol, (iii) the esterification of formic acid intermediate formed by oxidation of formaldehyde with methanol, and (iv) the dimerization of formaldehyde via Tish-chenko-type reaction.[40] Kominami et al. proposed that the photocatalytic oxidation of methanol to methyl formate mainly proceeds through the intermediate of formaldehyde followed by its thermal-activated dimerization.[38] We performed controlled experiments of adsorption and (thermal/photocatalytic) reaction of formaldehyde and coadsorption and (thermal/photocatalytic) reaction of formaldehyde and methanol on the $TiO_2(110)$ surface. Figure 6B shows TDS spectra after the $TiO_2(110)$ surface was exposed to 0.01 L HCHO at 110 K. Besides the molecular desorption of formaldehyde at 288 K, only a weak desorption trace of C_2H_4 was observed at 690 K that arises from the subsurface Ti interstitials or surface oxygen vacancies-mediated coupling reaction of formaldehyde on $TiO_2(110)$ surface.[41,42] Figure 6C shows TDS spectra after the $TiO_2(110)$ surface was exposed to 0.01 L HCHO at 110 K followed by a UV-light irradiation for 20 min. As compared to Figure 6B, the desorption trace of m/z = 27 grows and broadens, demonstrating that the UV-light irradiation can induce surface reactions of formaldehyde on the $TiO_2(110)$ surface, which will be discussed elsewhere. No formation of formic acid and methyl formate was observed during the adsorption and (thermal/photocatalytic) reaction of formaldehyde on the $TiO_2(110)$ surface at 110 K. Figure 7A shows TDS spectra after the $TiO_2(110)$ surface was exposed to 0.42 ML methanol and subsequently to 0.01 L HCHO at 110 K. The desorption traces of methanol and formaldehyde dominate the TDS spectra, and the formation of methyl formate (m/z = 60) was not observed. Figure 7B shows TDS spectra after the $TiO_2(110)$ surface was exposed to 0.42 ML methanol and subsequently to 0.01 L HCHO at 110 K followed by a UV-light irradiation for 5 min. Besides the desorption traces of methanol and formaldehyde, the desorption trace of methyl formate (m/z = 60) was clearly observed at ~220 K. The results of these controlled experiments unambiguously prove that methyl formate is formed on the $TiO_2(110)$ surface at 110 K by the photocatalytic cross-coupling of formaldehyde and methanol instead of dimerization of formaldehyde proposed by Kominami et al.[38] Therefore, the formation of methyl formate during the photocatalytic oxidation of methanol on the $TiO_2(110)$ surface consists of two sequential photocatalytic reactions (Figure 8): the photocatalytic oxidation of methanol to formaldehyde followed by the photocatalytic cross-coupling of formaldehyde and methanol. Concerning the photocatalytic cross-coupling mechanism, Phillips et al.[35] proposed the involvement of a transient HCO intermediate made photochemically from formaldehyde, but Guo et al.[36] argued that such a transient HCO intermediate was not necessary. Because all of the photocatalytic oxidation reactions occur on the $TiO_2(110)$ surface at 110 K, the photocatalytic cross-coupling between aldehydes and alcohols catalyzed by TiO_2 should be facile and might be developed to a novel green and benign route to synthesize esters directly from alcohols or from alcohols and aldehydes.

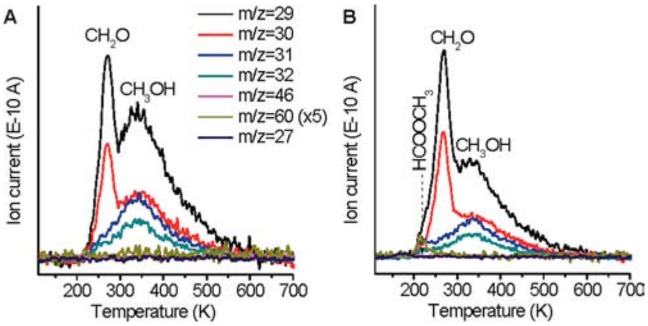

Figure 7. (A) TDS spectra after the $TiO_2(110)$ surface was exposed to 0.42 ML methanol and then to 0.01 L HCHO at 110 K. (B) TDS spectra after the $TiO_2(110)$ surface was exposed to 0.42 ML methanol and then to 0.01 L HCHO at 110 K followed by a UV-light irradiation for 5 min.

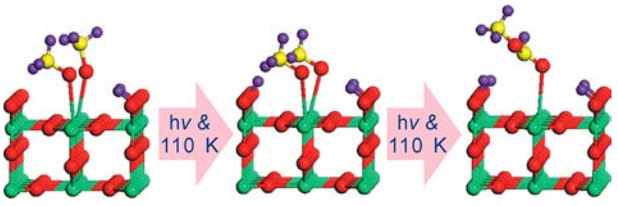

Figure 8. Schematic illustration of the photocatalytic oxidation of methoxy species to formaldehyde and the subsequent photocatalytic cross-coupling of methoxy species and formaldehyde to methyl formate on the $TiO_2(110)$ surface covered with methanol. The red, green, yellow, and purple spheres represent O, Ti, C, and H atoms, respectively.

Our TDS results (Figure 3) demonstrate the photocatalytic oxidation of methanol to formaldehyde dominates the initial 1 min of photocatalytic oxidation of methanol on the $TiO_2(110)$ surface; thus the decrease of the C 1s peak at 286.9 eV and the appearance and growth of the C 1s peak at 288.4 eV in the corresponding XPS results (Figure 5A and B) suggest the formation of formaldehyde by the photocatalytic oxidation of methoxy species on the surface. These observations agree with previous reports[27,30] that chemisorbed methoxy species on the Ti^{4+} sites of $TiO_2(110)$ surface is the active species in the photocatalytic oxidation of methanol to formaldehyde. Beyond 1 min, both photocatalytic oxidation of methanol to formaldehyde and photocatalytic cross-coupling of methanol and formaldehyde occur on the surface, and the C 1s peak at 288.4 eV in the XPS spectra contributed by both formaldehyde and methyl formate reasonably keeps growing, but the C 1s peak at 286.9 eV in the XPS spectra contributed by both methoxy species and methyl formate does not decrease as expected because the methoxy species continuously gets supplied by the dissociation of chemisorbed methanol (Figure 5A and B). The dissociation of chemisorbed methanol on the Ti^{4+} sites of $TiO_2(110)$ surface to the methoxy species during the photocatalytic oxidation of methanol on the $TiO_2(110)$ surface occurs via two likely mechanisms: one is that the photocatalytic oxidation of methoxy species shifts the thermal equilibrium between chemisorbed methanol and methoxy species toward the formation of methoxy species, as proposed by Henderson et al.;[27,30,31] the other is the photocatalytic dissociation of chemisorbed methanol to the methoxy species as proposed by Yang et al.[24,29,32] Because our XPS results provide the relative surface coverage variation of different surface species during the photocatalytic oxidation of methanol on the $TiO_2(110)$ surface (Figure 5B), we performed the following preliminary reaction kinetic analysis to elucidate the mechanism of the dissociation of chemisorbed methanol from the Ti^{4+} sites of $TiO_2(110)$ surface to methoxy species.

Model I. Assuming that the dissociation of chemisorbed methanol to methoxy species is only thermally controlled at 110 K, it is plausible that the activation energy of the thermal dissociation reaction is low and the chemisorbed methanol and methoxy species are in thermal equilibrium.[27,30,31] Thus, the photocatalytic oxidation of methanol on the $TiO_2(110)$ surface can be described as follows (O_{br} means the bridging-bonded O sites of the $TiO_2(110)$ surface):

$$CH_3OH(a) + O_{br} \overset{K}{\leftrightarrow} CH_3O(a) + O_{br}H$$

$$CH_3O(a) + O_{br} \xrightarrow{h\nu, r_2} HCHO(a) + O_{br}H$$

$$CH_3O(a) + HCHO(a) + O_{br} \xrightarrow{h\nu, r_3} HCOOCH_3(a) + O_{br}H$$

The surface coverage change of different surface species can be expressed as follows:

$$\frac{d[CH_3O(a)]}{dt} = 0$$

$$\frac{d[HCHO(a)]}{dt} = r_2 - r_3$$

$$\frac{d[HCOOCH_3(a)]}{dt} = r_3$$

The peak intensity change of different C 1s features can be expressed as follows:

$$\frac{dI(288.4\ \mathrm{eV})}{dt} = \frac{d[HCHO(a)]}{dt} + \frac{d[HCOOCH_3(a)]}{dt} = r_2$$

$$\frac{dI(286.9\ \mathrm{eV})}{dt} = \frac{d[CH_3O(a)]}{dt} + \frac{d[HCOOCH_3(a)]}{dt} = r_3$$

Model II. Assuming that the dissociation of chemisorbed methanol to the methoxy species is photocatalytic, the photocatalytic oxidation of methanol on the $TiO_2(110)$ surface can be described as follows:

$$CH_3OH(a) + O_{br} \xrightarrow{h\nu, r_1} CH_3O(a) + O_{br}H$$

$$CH_3O(a) + O_{br} \xrightarrow{h\nu, r_2} HCHO(a) + O_{br}H$$

$$CH_3O(a) + HCHO(a) + O_{br} \xrightarrow{h\nu, r_3} HCOOCH_3(a) + O_{br}H$$

The surface coverage change of different surface species can be expressed as follows:

$$\frac{d[CH_3O(a)]}{dt} = r_1 - r_2 - r_3$$

$$\frac{d[HCHO(a)]}{dt} = r_2 - r_3$$

$$\frac{d[HCOOCH_3(a)]}{dt} = r_3$$

The peak intensity change of different C 1s features can be expressed as follows:

$$\frac{dI(288.4\ \mathrm{eV})}{dt} = \frac{d[HCHO(a)]}{dt} + \frac{d[HCOOCH_3(a)]}{dt} = r_2$$

$$\frac{dI(286.9\ \mathrm{eV})}{dt} = \frac{d[CH_3O(a)]}{dt} + \frac{d[HCOOCH_3(a)]}{dt} = r_1 - r_2$$

The reaction kinetics following model I suggests that both the C 1s feature at 286.9 eV and the C 1s feature at 288.4 eV should increase with the prolonging of the irradiation time, while that following model II suggests that with the prolonging of the irradiation time, the C 1s feature at 288.4 eV should increase and the peak intensity of the C 1s feature at 286.9 eV should depend on the reaction rates r_1 and r_2. As compared to the results shown in Figure 5B, particularly with the peak intensity change of the C 1s feature at 286.9 eV, model II is reasonable but model I is not. Therefore, our results clearly demonstrate that the photocatalytic dissociation of chemisorbed methanol on the Ti^{4+} sites of $TiO_2(110)$ surface to the methoxy species occurs and contributes to the photocatalytic oxidation of methanol on $TiO_2(110)$ surface, although the thermal dissociation mechanism cannot be excluded.

Phillips et al.[35] have just reported the sequential photooxidation of methanol to methyl formate on $TiO_2(110)$ covered with O adatoms by means of thermal desorption spectroscopy (TDS), scanning tunneling microscopy (STM), and theoretical calculations. Very recently, Guo et al.[36] reported the formation of methyl formate as the product of photooxidation of methanol on bare $TiO_2(110)$ by means of TDS. As compared to their work[35,36] in which the sequential photooxidation of methanol to methyl formate on the $TiO_2(110)$ surface was evidenced by means of TDS, our results are still of great significance and novelty. First, our XPS results clearly demonstrate the evolution of various surfaces species during the photocatalytic oxidation of methanol on the $TiO_2(110)$ surface and thus provide direct and unambiguous spectroscopic evidence for the formation of methyl formate as the product of photocatalytic cross-coupling of chemisorbed formaldehyde with chemisorbed methoxy species. Second, in Phillips et al.'s work,[35] the exposure of the employed $TiO_2(110)$ surface to O_2 was needed for the occurrence of the photooxidation of methanol to methyl formate, but in both Guo et al.'s work[36] and our case such a pretreatment of $TiO_2(110)$ surface is not required. Phillips et al. proposed that the exposure of the $TiO_2(110)$ surface to O_2 acts to heal the $TiO_2(110)$ surface and that the O adatoms formed on $TiO_2(110)$ surface by O_2 exposure are not required for the photocatalytic reactions. As evidenced by the formation of $CH_3O(a)$ upon methanol adsorption and the formation of ethylene upon formaldehyde adsorption, our rutile $TiO_2(110)$ sample is also with certain amounts of bulk defects and surface oxygen vacancies; however, the photooxidation of methanol to formaldehyde and methyl formate could occur without pretreatment. Thus, it seems that the density of bulk defects in $TiO_2(110)$ surface strongly affects the efficiency of the photocatalytic oxidation reactions of methanol. The light absorption and photoexcitation processes mainly occur in the bulk of $TiO_2(110)$ sample; thus the bulk defects can serve as hole traps that severely suppress the participation of the holes into the photooxidation reaction occurring on the $TiO_2(110)$ surface. Third, our results clearly demonstrate that the photocatalytic dissociation of chemisorbed methanol on the Ti^{4+} sites of $TiO_2(110)$ surface to the methoxy species occurs and contributes to the photocatalytic oxidation of methanol on the $TiO_2(110)$ surface.

We have also compared the yield of methyl formate in the photocatalytic oxidation of methanol on the $TiO_2(110)$ surfaces covered with different amounts of adsorbed methanol (Figure 9). The yield increases as the coverage of adsorbed methanol increases from 0.15 to 0.42 ML; thus the increase of methanol chemisorbed on the Ti^{4+} of $TiO_2(110)$ is beneficial to the photocatalytic oxidation of methanol, supporting that methanol chemisorbed on the Ti^{4+} of $TiO_2(110)$ is the photocatalytic active species. However, further increase of the coverage of adsorbed methanol from 0.42 to 0.97 ML results in the reduction of the yield of methyl formate, suggesting that the presence of $CH_3OH(a)$ chemisorbed on the bridging-bonded O sites of $TiO_2(110)$ surface should suppress the photocatalytic oxidation of methanol. A likely reason is that the adsorption of methanol on the bridging-bonded O sites of $TiO_2(110)$ surface reduces the number of vacant bridging-bonded O sites available for the formation of surface hydroxyl, another surface intermediate formed in both the photocatalytic oxidation of methoxy species to formaldehyde and the photocatalytic cross-coupling of methoxy groups and formaldehyde. The desorption temperature of methyl formate from the surface was found to shift to the low temperature with the increase of methanol coverage, which could be attributed to the increasing repulsive interaction among surface adsorbates.

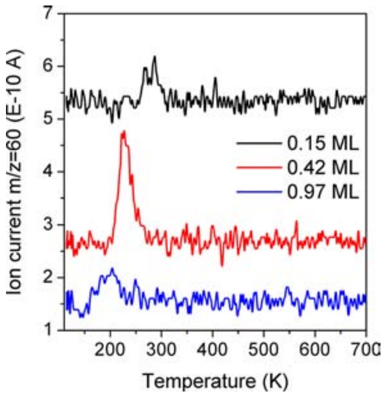

Figure 9. TDS spectra of methyl formate (m/z = 60) after the $TiO_2(110)$ surfaces covered with 0.15, 0.42, and 0.97 ML methanol were irradiated by a UV-light for 20 min.

4. CONCLUSIONS

In summary, we have successfully identified methyl formate as well as formaldehyde to be the products of the photocatalytic oxidation of methanol on the rutile $TiO_2(110)$ surface. Direct spectroscopic evidence has been provided for the first time to unambiguously prove the formation of methyl formate as the product of the photocatalytic cross-coupling of chemisorbed formaldehyde with chemisorbed methoxy species and to clearly demonstrate that the photocatalytic dissociation of chemisorbed methanol to methoxy species on the Ti^{4+} sites of $TiO_2(110)$ surface occurs and contributes to the photocatalytic oxidation of methanol on the $TiO_2(110)$ surface. Our findings are valuable not only in the molecular-level understanding of photocatalytic reactions over TiO_2-based photocatalysts, but also in the development of a green and benign photocatalytic route for the synthesis of esters directly from alcohols or from alcohols and aldehydes.

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Notes

The authors declare no competing financial interest.

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