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Methyl Formate Production on TiO_2(110), Initiated by Methanol Photocatalysis at 400 nm

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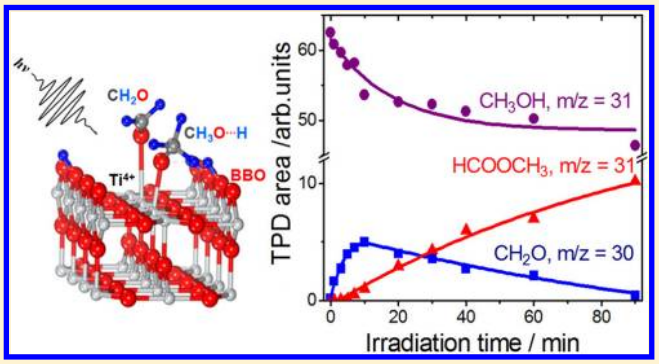
Supporting Information

ABSTRACT: Previous observations of methyl formate ($HCOOCH_3$) during the photo-oxidation of methanol (CH_3OH) on TiO_2 catalysts suggested that photocatalysis on TiO_2 could be used to build up complex molecules from a single precursor. We have investigated the mechanism of $HCOOCH_3$ formation by irradiating a CH_3OH-adsorbed TiO_2(110) surface with 400 nm light at low surface temperatures. Through the detection of volatile products after irradiation by temperature programmed desorption, we have found, as previously reported [Phillips et al. *J. Am. Chem. Soc.* **2013**, *135*, 574−577] that $HCOOCH_3$ is formed by the cross-coupling reaction of CH_3O and CH_2O, which are products of the first and second dissociation steps, respectively, in the stepwise photocatalysis of CH_3OH on TiO_2(110). Unlike the previous study, we have observed the photocatalytic production of $HCOOCH_3$ without preoxidation of the surface, and we have concluded that the final reaction step to produce $HCOOCH_3$ (i.e., the cross-coupling reaction of CH_2O with CH_3O) does not involve a transient HCO intermediate.



I. INTRODUCTION

The potential value of TiO_2 in biomass conversion into fuels and useful synthetic chemicals[1−7] has inspired enormous interest in replacing current technology for stoichiometric oxidation of alcohols[8] with photocatalytic processes on TiO_2 that could reduce energy consumption, minimize environmental pollutants, and increase selectivity.[9−13] Although CH_3OH is often used in benchmark studies of the photocatalytic properties of TiO_2,[2,7,14−21] there have been only a few studies on selective oxidation of CH_3OH over TiO_2 photocatalysts.[3,4,14,15,19,22] Various products were observed, such as H_2, CO, CO_2, CH_2O, HCOOH, and $HCOOCH_3$, but the mechanisms of methanol photo-oxidation remain unclear. The presence of $HCOOCH_3$ (methyl formate) suggests that synthetic reactions, catalyzed on surfaces by light, could be used to build complex molecules from a single precursor. In a recent study employing temperature programmed desorption (TPD) and scanning tunneling microscopy (STM), Friend and co-workers have deduced the mechanism of CH_3OH photo-oxidation on a preoxidized TiO_2(110) surface.[23] They concluded that coadsorbed oxygen atoms first reacted thermally with CH_3OH to produce adsorbed CH_3O and H_2O. Then CH_3O underwent photo-oxidation to $HCOOCH_3$ in a two-step process where the CH_3O dissociated to CH_2O and a cross-coupling reaction involving an HCO intermediate led to the formation of $HCOOCH_3$. In this study, the preoxidation of the surface was considered to be essential to the initial formation of adsorbed CH_3O, and the HCO intermediate was an indication of the hole-mediated dissociation of CH_2O by a bridge-bonded oxygen (BBO) atom.

Our earlier TPD study of CD_3OH photo-oxidation on TiO_2(110) described the stepwise dissociation to CD_3O and CD_2O in the absence of coadsorbed oxygen.[24] We have extended these experiments and have observed methyl formate production with a significant isotope effect. The photocatalytic transformation of CH_3OH into $HCOOCH_3$ on TiO_2(110) proceeds rapidly, while that of CD_3OH is negligible on the time scales studied. The use of isotopic substitution to stop the photo-oxidation process before the final coupling step to produce methyl formate has allowed us to demonstrate that the formyl species (HCO/DCO) is not an intermediate in this step, thus calling into question the hole-mediated dissociation mechanism of formaldehyde.

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Clean TiO_2(110) surfaces were dosed, typically at 120 K, with various coverages of precursor molecules before irradiation with 400 nm light, and products were detected by TPD subsequent to irradiation or by a time-of-flight (TOF) method during irradiation. Several experiments were performed in order to verify the cross-coupling mechanism starting from a single CH_3OH precursor on a pristine TiO_2(110) surface and to probe the possible formyl intermediate in the cross-coupling step.

II. EXPERIMENTAL DETAILS

The TPD apparatus has been described previously.[24] The base pressure of the sample chamber is $<6 \times 10^{-11}$ Torr. A quadrupole mass spectrometer (Extrel) is used to detect desorbed products. An extremely high vacuum of 1.5×10^{-12} Torr in the electron-impact ionization region was achieved and maintained during the experiment. The TiO_2(110) (Princeton Scientific) sample had dimensions of 10 mm × 10 mm × 1 mm. The surface was cleaned by cycles of Ar^+ sputtering and resistive heating to 850 K in vacuum; 1000 eV Ar^+ was used for the initial cycles until impurities of Ca, Na, K, and C were no longer observed by Auger electron spectroscopy. For subsequent cycles, 500 eV Ar^+ was used to flatten the surface. The TiO_2(110) surface contained 3−4% O-vacancy defects as determined by H_2O TPD.[25] CH_3OH (Aldrich, 99.9+ %) was further purified by several freeze−pump−thaw cycles before use and introduced into the sample chamber with a calibrated molecular beam doser. The surface temperature was maintained at 120 K during CH_3OH dosing, and it typically rose to ∼180 K during subsequent irradiation. The irradiating light came from a frequency doubled Ti:Sapphire femtosecond laser at 400 nm (Coherent, repetition rate 1 kHz). Unless otherwise stated, the average intensity of the laser beam on the sample was 400 mW with a diameter of 6 mm, corresponding to about 1.44×10^{18} photons cm^{-2} s^{-1}. The light was incident on the TiO_2(110) at ∼30° with respect to TiO_2(110) surface. TPD signals were collected after irradiation with a heating rate of 2 K/s and with the sample facing the mass spectrometer detector. To exclude effects from nonlinearity that might result from the relatively high photon fluxes used, we studied the power dependence of the primary CH_2O and secondary $HCOOCH_3$ products that were detected in our experiments (see Figure S1 of Supporting Information). We have observed no evidence that the photon fluxes used in our experiments would impart any anomalous behavior in our results arising from multiphoton effects.

III. RESULTS AND ANALYSIS

Figure 1 shows TPD spectra collected at the CH_2O parent mass-to-charge ratio, m/z = 30, corresponding to various irradiation times. Dissociative ionization of CH_3OH in the electron-impact ionizer may lead to a signal at m/z = 30, as evidenced by the TPD peak near 290 K when no UV irradiation is used.[10] Note that the CH_3OH desorption TPD spectrum does not show a peak at 640 K unless the surface is predosed with O_2.[10,23,26] After 400 nm irradiation, a peak appears at 260 K in the TPD spectrum and first increases and then decreases in magnitude with increasing irradiation time. This peak is assigned to CH_2O based on earlier studies from our lab[24] and others.[25,27] The near disappearance of this peak after an irradiation time of 90 min might be explained by photoinduced desorption or chemical conversion of CH_2O.

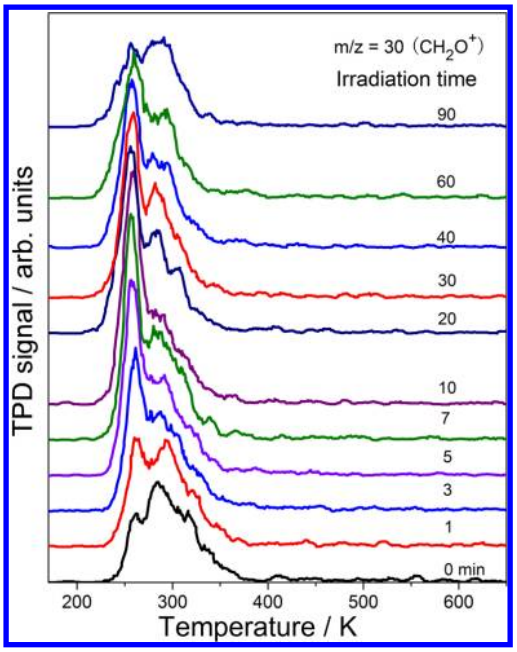

Figure 1. TPD spectra acquired at m/z = 30 after 0.5 ML of CH_3OH was adsorbed on TiO_2(110) at 120 K and irradiated at 400 nm for various times, as indicated.

To determine whether conversion to $HCOOCH_3$ was the reason for the disappearance of CH_2O, we collected TPD spectra at m/z = 31(CH_3O^+) for various irradiation times (see Figure 2). This m/z ratio was selected because it conveys a

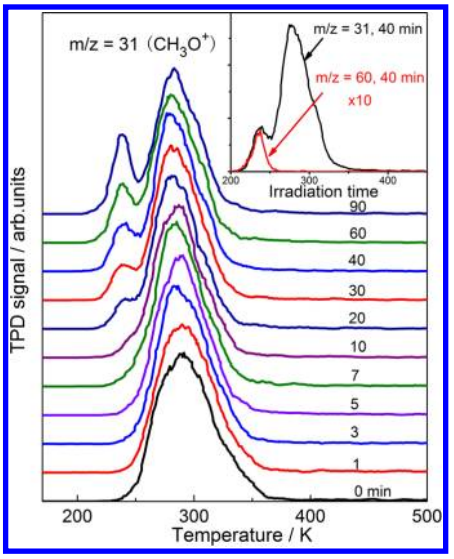

Figure 2. TPD spectra acquired at m/z = 31 after 0.5 ML of CH_3OH was adsorbed on TiO_2(110) at 120 K and irradiated at 400 nm for various times, as indicated. Inset shows a comparison between TPD spectra acquired at m/z = 31 and 60 after 40 min of irradiation time. We typically observe no CH_3OH TPD peak at 350 K with the Ar^+ sputtering conditions used in our experiments.

signal from all CH_3O-containing species that may dissociatively ionize, such as CH_3OH and $HCOOCH_3$. The main TPD peak, centered at 290 K, comes from CH_3OH. As the irradiation time increases, the CH_3OH TPD peak decreases in intensity and shifts toward lower temperatures, which was discussed in our earlier paper.[24] At longer irradiation times, a second peak

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appears as a shoulder at low temperatures, near 235 K, and increases in magnitude with increasing irradiation time. This low-temperature shoulder has the same TPD temperature and shape as the only peak observed in the m/z = 60 TPD spectrum (see inset in Figure 2), which corresponds to the parent m/z ratio of $HCOOCH_3^+$. However, according to ESD work involving CH_3OH on Ag(111) by Schwaner and White,[28] the m/z = 60 peak could arise from $HOCH_2CHO$ (glycolaldehyde) or $HCOOCH_3$.

Additional TPD traces help to distinguish between the two possible products detected at m/z = 60. TPD traces for m/z = 15(CH_3^+), 18(H_2O^+), 28(CO^+), 29(CHO^+), 30(CH_2O^+), and 32(CH_3OH^+) were measured following an irradiation time of 30 min (see Figure S2, Supporting Information). All TPD spectra show the appearance of an additional peak near 235 K after irradiation, except for the spectrum collected at m/z = 18. The lack of an additional m/z = 18 peak following laser irradiation leads to the conclusion that the product that desorbs at 235 K is $HCOOCH_3$ and not $HOCH_2CHO$.[29]

Figure 3 shows a comparison of the rates of destruction of CH_3OH and formation of CH_2O and $HCOOCH_3$ by showing

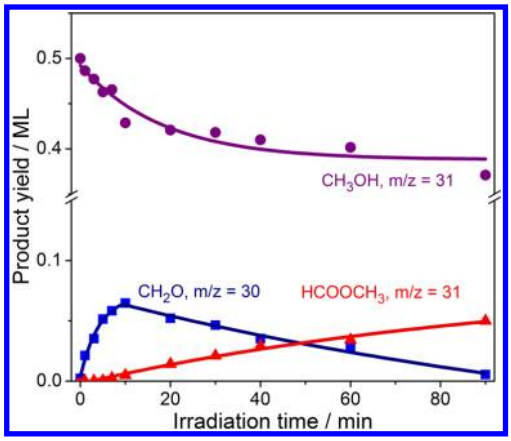

Figure 3. Yields of CH_3OH, CH_2O, and $HCOOCH_3$ as a function of irradiation time, derived from data in Figures 1 and 2.

the yields of these species as a function of irradiation time for 0.5 ML of CH_3OH adsorbed initially on TiO_2(110). Figure S3, Supporting Information, shows the yields for the analogous deuterated species when 0.5 ML of CD_3OH is adsorbed initially on TiO_2(110), where the $DCOOCD_3$ yield has been included with the already published yields of CD_3OH and CD_2O.[24] As can been seen in Figure 3, during the first 10 min of irradiation, the amount of CH_2O produced rises rapidly to a maximum, while hardly any $HCOOCH_3$ is formed. Longer irradiation times lead to a steady decrease in the amount of CH_2O and a concomitant increase in the amount of $HCOOCH_3$. After 90 min of irradiation, very little CH_2O remains. Thus, the formation of $HCOOCH_3$ appears to be directly correlated with the depletion of CH_2O. The rate of methyl formate formation exhibits a significant isotope effect. As shown in Figure S3, Supporting Information, when CD_3OH is used as the precursor, the yield of $DCOOCD_3$ is negligible on the time scales used in our experiments.

To confirm that the formation of $HCOOCH_3$ proceeds through coupling reactions involving CH_2O, we studied the dependence of the $HCOOCH_3$ TPD signal on the initial coverage of CH_3OH (see Figure 4, which shows a summary of the data presented in Figure S4, Supporting Information). After

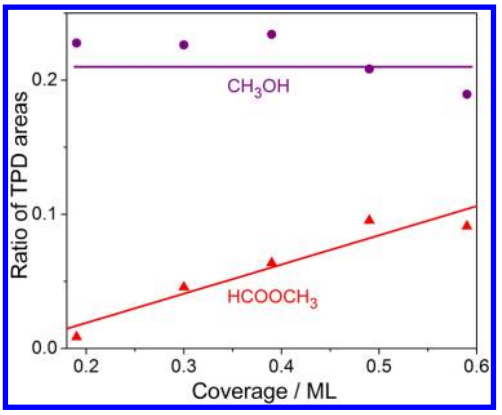

Figure 4. CH_3OH and $HCOOCH_3$ signals acquired at m/z = 31 as a function of initial CH_3OH coverage on a TiO_2(110) surface, with 30 min of 400 nm irradiation. At each coverage, the CH_3OH and $HCOOCH_3$ signals shown are ratios of the integrated TPD signals for the respective species to the integrated TPD signal of CH_3OH acquired at m/z = 31 without irradiation.

30 min of irradiation time, the TPD yield for CH_3OH decreases by roughly 20−22% regardless of its initial coverage, whereas the $HCOOCH_3$ signal, normalized to the initial coverage of CH_3OH, increases roughly linearly with the initial coverage of CH_3OH. On the basis of previous studies, the saturated first layer adsorption of CH_3OH on TiO_2(110) varies between 0.67 and 0.77 ML,[10,30] which implies that there are two adsorbed CH_3OH molecules per three Ti^{4+} sites or three adsorbed CH_3OH molecules per four Ti^{4+} sites when the first layer of adsorption is saturated. With increasing CH_3OH coverage, the $HCOOCH_3$ yield increases together with the probability of two CH_3OH molecules being adsorbed nearby each other. Thus, the clear dependence of $HCOOCH_3$ yield on CH_3OH coverage, combined with the anticorrelation between CH_2O and $HCOOCH_3$ product yields at long irradiation times (see Figure 3), strongly suggests that $HCOOCH_3$ formation is the result of coupling reactions between CH_2O and another reactive species that is connected with the initial presence of CH_3OH. Irradiation of the surface by 400 nm light produces CH_2O, which is evidently involved in the production of $HCOOCH_3$.

A series of thermal catalytic investigations on gas-phase dehydrogenation of CH_3OH to $HCOOCH_3$ over copper-based catalysts[31−34] concluded that the formation of $HCOOCH_3$ in the absence of O_2 occurs either through a hemiacetal (reaction of CH_3OH or CH_3O with CH_2O) or a Tishchenko (reaction of two CH_2O molecules) mechanism. The recent work of Friend and co-workers on the photo-oxidation of CH_3OH on a preoxidized Ti(110) surface suggests that $HCOOCH_3$ is formed exclusively through the cross-coupling reaction of CH_3O and CH_2O intermediates.[23] Both CH_3O and CH_2O are also available under our experimental conditions, as we have recently shown that CH_2O is formed through the stepwise photocatalysis of CH_3OH on TiO_2(110), with CH_3O as the intermediate species. Indeed, through an experiment involving surfaces on which CH_3OH and CD_3OH were coadsorbed, we found that the cross-coupling reaction occurs (see Figure 5), and in a separate experiment that started with adsorbed CH_2O, we saw no evidence for formation of $HCOOCH_3$, indicating that the self-coupling reaction does not occur (Figure 6). Thus, we conclude that the cross-coupling reaction also proceeds

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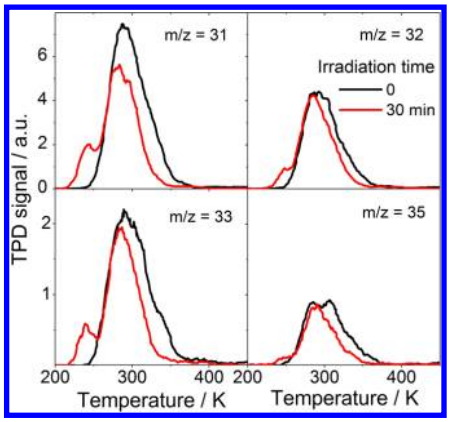

Figure 5. TPD spectra acquired at m/z = 31(CH_3O^+, $CHDO^+$), 32(CH_4O^+, CH_2DO^+, CD_2O^+), 33(CHD_2O^+, CH_3DO^+), and 35-(CHD_3O^+) after 0.35 ML of CH_3OH and 0.15 ML of CD_3OH were coadsorbed on TiO_2(110) at 105 K and irradiated at 400 nm for 0 (black) and 30 min (red). CD_3OH was dosed first. The m/z ratios correspond to fragments of various possible isotopic variants of methanol, formaldehyde, and methyl formate. In all these spectra, the large peaks at ~290 K arise from desorption of methanol, and the shoulders at lower temperatures may come from either formaldehyde or methyl formate. The shoulder in the TPD spectrum collected at m/z = 35 could only come from a fragment of $HCOOCD_3$, formed from a cross-coupling reaction of CH_2O and CD_3O. Thus, the cross-coupling reaction clearly occurs.

exclusively under our experimental conditions, with irradiation at 400 nm.

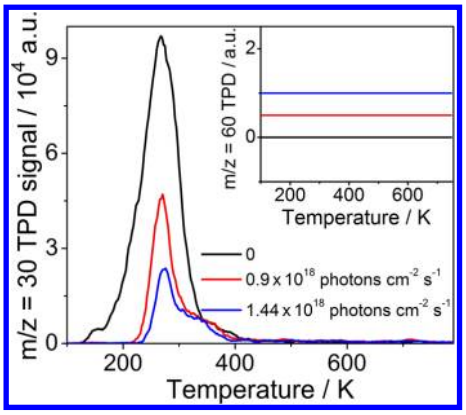

Figure 6. TPD spectra acquired at m/z = 30(CH_2O^+) after 0.55 ML of CH_2O was dosed on TiO_2(110) and either not irradiated or irradiated with different photon fluxes, as shown, for 30 min. The inset shows that no TPD signal was observed at m/z = 60($HCOOCH_3^+$) under any of these conditions. The lack of $HCOOCH_3$ indicates that the self-coupling reaction of CH_2O does not occur.

An experiment with coadsorbed CH_3O and CH_2O was performed to verify that the cross-coupling reaction was photocatalyzed and occurred during irradiation, rather than during TPD via a thermal mechanism. As shown in Figure 7, with 0.14 ML of CH_3O and 0.5 ML of CH_2O initially coadsorbed on the TiO_2(110) surface, no $HCOOCH_3$ signal could be observed during TPD of the unirradiated surface. Thus, heating does not promote the reaction on a TiO_2(110) surface. Note that the coupling of CH_3O and CH_2O does, however, occur thermally on a Au(111) surface.[35−39]

H atoms were also detected (via TPD of H_2O) from irradiation of CH_3OH-adsorbed TiO_2(110), and their coverage

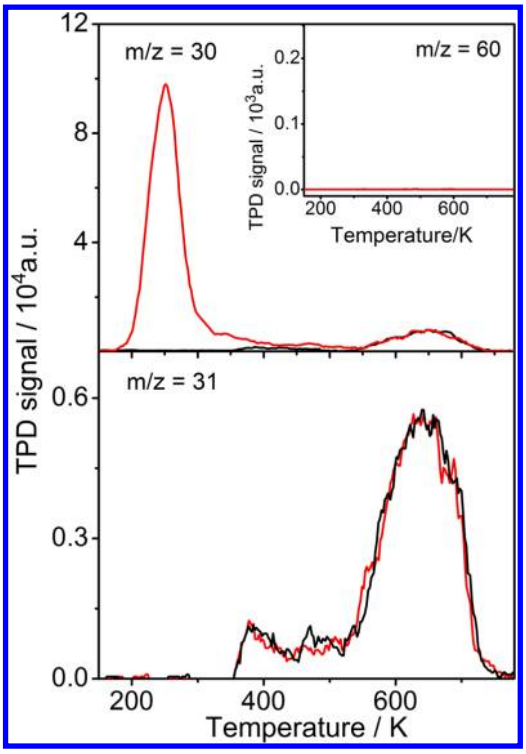

Figure 7. TPD spectra acquired at m/z = 30(CH_2O^+), m/z = 31(CH_3O^+), and m/z = 60($CH_4O_2^+$) from 0.14 ML of CH_3O adsorbed on TiO_2(110) (black line) and 0.14 ML of CH_3O and 0.5 ML of CH_2O coadsorbed on TiO_2(110) (red line). Surface methoxy groups were produced by sequential dosing of oxygen and methanol gases, followed by flashing the sample to 350 K to remove water and molecularly adsorbed methanol.[10,26] As shown in the inset, no signal at m/z = 60($HCOOCH_3^+$) was observed with CH_2O and CH_3O coadsorbed on a TiO_2(110) surface, implying that the cross coupling reaction to produce $HCOOCH_3$ was photocatalyzed and did not occur thermally during TPD. The 640 K peak in both TPD spectra arises from CH_3O disproportionation, as has been discussed previously.[26]

corresponds mainly to H atoms produced by dissociation of CH_3OH as it underwent the loss of two H atoms to form CH_2O. Before irradiation, the H-atom coverage was about 0.03 ML. After 90 min of irradiation, 0.24 ML of H atoms on BBO sites remained (Figure 8), consistent with the 0.13 ML of CH_3OH depletion observed in Figure 3. A tiny amount of H_2 might have been produced from recombination, but these signals were below our detection limit.

As depicted in Figure 6, no $HCOOCH_3$ was observed after irradiation of the TiO_2(110) surface with adsorbed CH_2O, even though a large fraction of the CH_2O coverage disappears during 30 min of irradiation. A small fraction of the CH_2O product desorbs during irradiation, as evidenced by a TOF signal of CH_2O (Figure 9), which corresponds to desorption of ~0.01 ML during the first 30 min of irradiation. Most of the disappearance of CH_2O appears to be from conversion to formate, as revealed in the TPD spectra shown in Figure 10, which were collected at m/z = 28($C_2H_4^+$, CO^+), 29(CHO^+), 30(CH_2O^+), 44(CO_2^+), 45($HCOO^+$), and 46($HCOOH^+$). Two new desorption features at 486 and 587 K appear in the m/z = 29 TPD spectrum with 30 min of irradiation, suggesting that the new features are possibly the result of photocatalytic products. Using previous studies of HCOOH adsorbed on TiO_2(110)[40] and the cracking pattern of HCOOH collected with our mass spectrometer, we concluded that the 486 K peak

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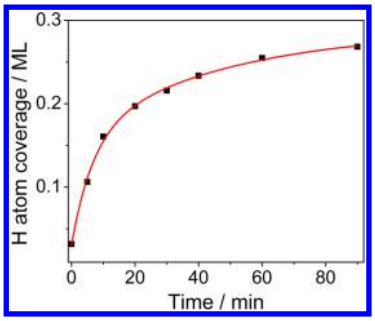

Figure 8. H-atom coverage on BBO sites as a function of irradiation time at 400 nm (laser flux = 1.44×10^{18} photons cm^{-2} s^{-1}) for 0.5 ML of CH_3OH adsorbed initially on $TiO_2(110)$. The decomposition of CH_3OH to CH_2O and $HCOOCH_3$ results in surplus H atoms, which transfer to BBO sites. During TPD, the H atoms combine with BBO atoms to produce desorbed H_2O. On the basis of the peak area of the first layer water desorption, the H-atom coverage on BBO sites can be determined from the measured peak area. It is clear from these data that the depletion of CH_3OH is the result of H-atom dissociation.

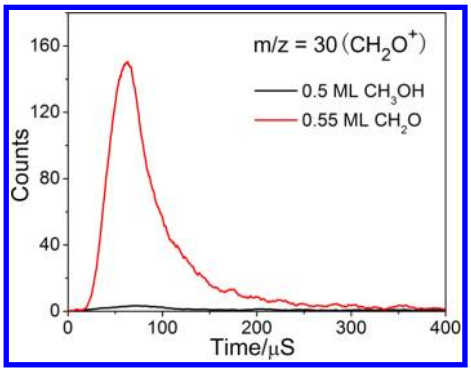

Figure 9. TOF signals of CH_2O, ejected from 0.55 ML[10,30] of CH_2O-adsorbed $TiO_2(110)$ (black line) and from 0.5 ML CH_3OH-adsorbed $TiO_2(110)$ during irradiation (red line). On the basis of quantitative coverages derived from the data shown in Figure 6, after 400 nm of irradiation for 30 min (with a laser flux of 1.44×10^{18} photons cm^{-2} s^{-1}), 0.08 ML of CH_2O was left on the surface, and about 0.15 ML of CH_2O transferred to other products, such as HCOOH, CH_3, and formates. From the areas of the TOF signals, we conclude that about 0.01 ML of CH_2O was desorbed during the first 30 min of irradiation of a $TiO_2(110)$ surface with 0.5 ML of CH_3OH adsorbed.

at m/z = 29, 44, 45, and 46 is desorbed HCOOH, which results from the recombination of surface formates with surface hydroxyl groups. The 587 K peak at m/z = 28, 29, and 44 is assigned to desorption of surface formates in the form of CO, HCO, and CO_2. Previous investigations on the photochemistry of acetone and acetaldehyde on preoxidized $TiO_2(110)$[41−47] show that acetone or acetaldehyde adsorbed on oxidized $TiO_2(110)$ undergoes a facile thermal reaction to form a photoactive acetone−oxygen or acetaldehyde−oxygen complex first, and then ultraviolet (UV) light irradiation of the acetone−oxygen or acetaldehyde−oxygen complex results in the ejection of methyl radical into gas phase and conversion of the surface bound fragment to acetate or formate. Here, without a preoxidized $TiO_2(110)$ surface, the main product, formate, was still observed in our experiments, implying that a photoactive H_2CO−O complex was formed during UV irradiation and suggesting that bridge-bonded O atoms are involved in the complex. Taking into account mass spectrometer sensitivity factors, the yield of CO is about 0.08 ML after 30 min of irradiation.

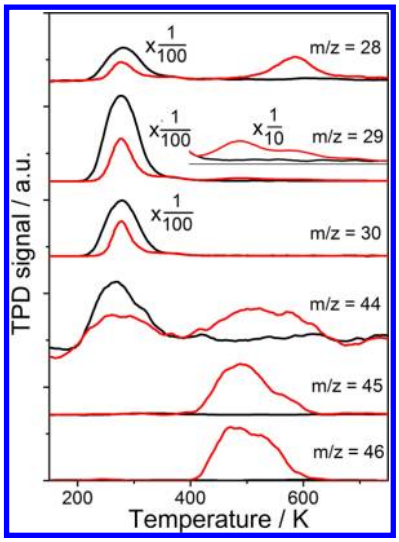

Figure 10. TPD spectra acquired at m/z = 28($C_2H_4^+$, CO^+), 29(CHO^+), 30(CH_2O^+), 44(CO_2^+), 45($HCOO^+$), and 46($HCOOH^+$) after 0.55 ML of CH_2O was adsorbed on $TiO_2(110)$ at 110 K and irradiated for 0 (black) and 30 min (red) with 400 nm light at 0.54×10^{18} photons cm^{-2} s^{-1}. The 486 K peak at m/z = 29, 44, 45, and 46 is desorbed HCOOH, which results from the recombination of surface formates with surface hydroxyl groups. The 587 K peak at m/z = 28, 29, and 44 is assigned to desorption of surface formates in the form of CO, HCO, and CO_2.

IV. DISCUSSION

Previous studies from our group[24] and others[48−50] indicate that the molecular state of methanol adsorbed on a Ti^{4+} site is nearly isoenergetic with the dissociated state (CH_3O + H) and that the barrier between these states is very low. Hence, the two states should coexist in equilibrium even at low surface temperatures. In order for the cross-coupling reaction to be promoted by heat, the CH_3O intermediate species would have to persist after irradiation. However, the easy back reaction, $CH_3O + H \rightarrow CH_3OH$, should remove CH_3O in the form of CH_3OH during TPD. Furthermore, the relatively easy forward reaction, $CH_3O \rightarrow CH_2O + H$ with UV radiation would make it very unlikely that CH_3O is available for cross-coupling reactions, especially after long irradiation times.[23−25] The facts that (1) CH_3O must be efficiently removed by back-reacting to CH_3OH during TPD and that (2) the yield of $HCOOCH_3$ increases with irradiation time are consistent with the conclusion that the cross-coupling reaction of CH_3O and CH_2O in our experiment occurs during irradiation and not when the surface is heated for the TPD measurement.

Recent thermal catalytic studies are consistent with a preference of cross-coupling over self-coupling. A study of CH_2O polymerization on $(WO_3)_3/TiO_2(110)$ shows that no $(CH_2O)_n$ desorption was observed on a bare $TiO_2(110)$ surface,[51] whereas thermal catalytic studies of $HCOOCH_3$ formation from CH_3OH on Au(111)[35−39] and PdO(101) thin films[52] all concluded that the cross-coupling reaction of CH_3O and CH_2O could occur below room temperature as a result of the easy attack of CH_2O by CH_3O. The earlier studies[51] also indicated that the barrier for CH_2O dimerization is higher than that for the cross-coupling reaction of CH_3O and CH_2O. In our experiment, CH_3O might be more likely to react with adjacent CH_2O than to dissociate to produce additional CH_2O because the presence of bridge-bonded H atoms could inhibit the dissociation reaction, $CH_3O \rightarrow CH_2O + H$. An

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increased likelihood for CH_3O to undergo a cross-coupling reaction than a dissociation reaction would prevent the build-up of CH_2O that would be available for self-coupling reactions. Indeed, Figure 3 suggests that the buildup of CH_2O is limited by the formation of $HCOOCH_3$.

Friend and co-workers have proposed that the formyl radical (HCO) is an intermediate in the mechanism by which CH_3O and CH_2O react on a surface to produce $HCOOCH_3$. HCO is presumably formed by the hole-mediated abstraction of an H atom by a BBO atom. The evidence for HCO comes from irradiating a surface of coadsorbed CH_2O and O. The observation of CO and CO_2 at high temperatures from a UV-irradiated $TiO_2(110)$ surface with coadsorbed CH_2O and O indicated the presence of formate and thus led to the conclusion that irradiation induces the loss of H, which would create an HCO intermediate. This conclusion is apparently at odds with an isotopic labeling study on the dehydrogenation of methanol to methyl formate over copper-based catalysts,[53] which ruled out an HCO intermediate in the coupling of methoxy and formaldehyde to form methyl formate. However, the different catalytic system might alter the mechanistic details. Nevertheless, the inference of an HCO intermediate based on formate formation is further called into question by recent investigations showing that a radical intermediate, RCO, is not required in the photoinduced transformation of acetone and acetaldehyde to formate on preoxidized $TiO_2(110)$.[41−47] These studies have demonstrated that acetone or acetaldehyde adsorbed on preoxidized $TiO_2(110)$ undergoes a facile thermal reaction to form a photoactive acetone−oxygen or acetaldehyde−oxygen complex first, and then UV light irradiation of the acetone−oxygen or acetaldehyde−oxygen complex results in the ejection of a methyl radical into the gas phase and conversion of the surface bound fragment to acetate or formate.

We, too, observe evidence for formate when CH_2O is adsorbed on a $TiO_2(110)$ surface and irradiated (see Figure 10). The fact the formate is produced from CH_2O without coadsorbed oxygen suggests that one of the O atoms in the formate species comes from a BBO row. Formation of formate from CH_2O in the absence of coadsorbed oxygen does not necessarily imply an HCO intermediate, but such an intermediate might be possible. If HCO were formed, then formate production in conjunction with BBO atoms would be expected to compete with other reactions.

The use of isotopic substitution can be used to show that HCO (or DCO) is not an intermediate in the cross-coupling reaction that produces $HCOOCH_3$ (or $DCOOCD_3$) under our experimental conditions. As seen in Figure S3, Supporting Information (and in our earlier study[24]), when CD_3OH is used as the methanol precursor, CD_2O builds up on the surface but reacts only negligibly with CD_3O to produce $DCOOCD_3$. Thus, the final cross-coupling step is effectively blocked by the isotope effect, allowing the investigation of the state of CD_2O on a surface that is representative of the actual reactive system. Figure 11 shows various TPD spectra from such a surface that started with 0.5 ML of adsorbed CD_3OH, with three irradiation durations. After 60 min of irradiation, about 0.13 ML of CD_3OH is depleted (not including the small fraction of CD_3OH that undergoes an isotope exchange to form CD_3OD or reaction with oxygen vacancy sites), implying that 0.13 ML of CD_2O is formed (including adsorbed and photodesorbed CD_2O). Unlike the TPD spectra collected when CH_2O was adsorbed on the surface and irradiated (Figure 10), the m/z = 28 TPD spectrum from a CD_3OH-adsorbed and irradiated

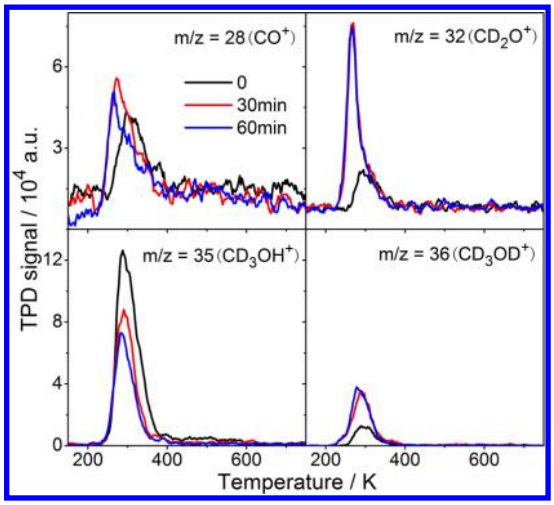

Figure 11. TPD spectra acquired at m/z = 28(CO^+), 32(CD_2O^+), 35(CD_3OH^+), and 36(CD_3OD^+) from 0.5 ML of CD_3OH adsorbed on $TiO_2(110)$, with irradiation times of 0, 30, and 60 min, as shown.

surface exhibits no peak at 587 K (Figure 11), demonstrating that formate is not formed on this surface. The absence of formate indicates that DCO could not have been formed, which strongly suggests that HCO is not an intermediate in the cross-coupling reaction to produce $HCOOCH_3$ on $TiO_2(110)$. The reaction probably proceeds through a direct coupling of CH_3O and CH_2O, as has been proposed earlier as part of a hemiacetal mechanism.[53]

The lack of apparent C−D bond dissociation from CD_2O on the CD_3OH-adsorbed surface vs C−H bond dissociation from CH_2O on the CH_2O-adsorbed surface might be explained by the availability of unoccupied BBO sites. When CD_3OH (or CH_3OH) undergoes stepwise photocatalytic dissociation, hydrogen atoms are transferred to BBO atoms. Thus, neighboring BBO sites would not be available to receive a hydrogen atom from CH_2O (or CD_2O), as they would be when only CH_2O is adsorbed on the surface. Even in a direct coupling mechanism, which does not involve an HCO intermediate, an H atom must be lost and inevitably go to a BBO site. Thus, at least one of the reactants, presumably CH_2O as a result of its relatively low adsorption energy, would be expected to require some mobility on the surface in order to react near a BBO site without an attached H atom. In an analogous TPD experiment conducted with irradiation at 355 nm, we have found that a modest increase in surface temperature dramatically enhances the production rate of $HCOOCH_3$ (Figure 12). The temperature-dependent production of $HCOOCH_3$ is consistent with the presumed requirement for surface mobility of CH_2O. Note that the surface temperature (180 K) at which $HCOOCH_3$ was observed to be formed is similar to the temperature (180 K) used in the experiment with CD_3OH from which we concluded that DCO (or HCO) cannot be an intermediate in the cross-coupling reaction. Thus, under conditions where there should be sufficient mobility to promote the cross-coupling reaction, we do not observe formate formation and can rule out the DCO (or HCO) intermediate. We therefore conclude that the mobility of CH_2O is not required to move it to a site where HCO can be formed; rather, we believe that it moves to a location where it can couple directly with CH_3O and lose its H atom to a BBO site. Instead of being mediated by hole formation on a BBO atom, as has been suggested,[23] the cross-

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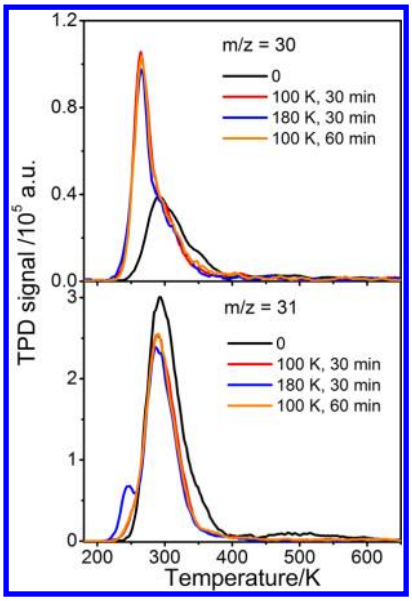

Figure 12. TPD spectra acquired at m/z = 30(CH_2O^+) and 31(CH_3O^+), from 0.5 ML of CH_3OH adsorbed on TiO_2(110), with irradiation at 355 nm. The laser flux was 1.27×10^{17} photons cm^{-2} s^{-1} with a bandwidth of ~20 nm and a spot size of 6 mm. Irradiation times are noted in the figure. TPD spectra from the unirradiated surface and the low-temperature-irradiated surfaces followed initial adsorption at 100 K. With the low UV flux used, the surface temperature rose less than 5 K during irradiation of the low-temperature surfaces. The surface was maintained at a temperature of 180 K for the higher temperature irradiation. The TPD spectra indicate that CH_3OH can be photocatalyzed to CH_2O at 100 or 180 K but that CH_2O only reacts to produce $HCOOCH_3$ at the higher temperature.

coupling reaction might simply occur on the ground electronic state, promoted by localized surface heating from photon irradiation.

V. CONCLUSIONS

Our TPD results show strong evidence that the cross-coupling reaction, $CH_3O + CH_2O \rightarrow HCOOCH_3 + H$, is concurrent with the stepwise photocatalytic dissociation of CH_3OH on rutile TiO_2(110) at an irradiation wavelength of 400 nm, where CH_3O and CH_2O are the products of the first and second steps and where initial coadsorption of oxygen is not necessary to initiate the process. This reaction takes place during irradiation, with longer irradiation times resulting in almost complete conversion of the CH_2O product into $HCOOCH_3$. The reaction does not appear to involve an HCO intermediate and may proceed through direct coupling of CH_3O and CH_2O through a hemiacetal mechanism. The conclusion that HCO is not an intermediate suggests that a hole-mediated mechanism might not be operable in this reaction. The observation that $HCOOCH_3$ may be formed from a single precursor (CH_3OH) by irradiation at low temperatures further demonstrates the utility of TiO_2 as a photocatalyst for synthetic reactions, especially the esterification of alcohols. Further utility in photocatalytic reactions should come from a detailed understanding of the dynamical processes at the surface that channel photon energy into the reaction coordinate.

■ ASSOCIATED CONTENT

Supporting Information

Dependence of TPD signals on laser photon flux. TPD spectra at a variety of m/z ratios, verifying that methyl formate is formed rather than glycolaldehyde. Yields of CD_2O and $DCOOCD_3$ when a CD_3OH-adsorbed TiO_2(110) surface is irradiated. Dependence of $HCOOCH_3$ TPD signal on initial coverage of CH_3OH. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

⊥These authors have made similar contributions to this work.

Notes

The authors declare no competing financial interest.

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