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Sequential Photo-oxidation of Methanol to Methyl Formate on $TiO_2(110)$

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Supporting Information

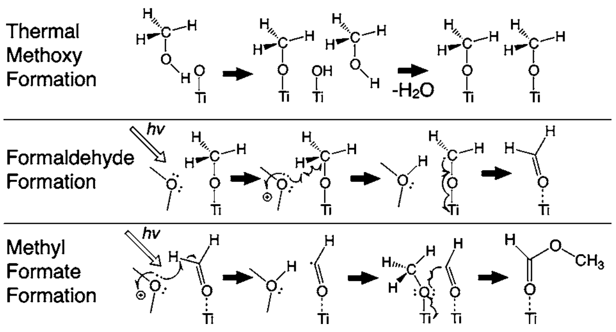
ABSTRACT: Methyl formate is produced from the photo-oxidation of methanol on preoxidized $TiO_2(110)$. We demonstrate that two consecutive photo-oxidation steps lead to methyl formate using mass spectrometry and scanning tunneling microscopy. The first step in methanol oxidation is formation of methoxy by the thermal dissociation of the O−H bond to yield adsorbed CH_3O and water. Formaldehyde is produced via hole-mediated oxidation of adsorbed methoxy in the first photochemical step. Next, transient HCO is made photochemically from formaldehyde. The HCO couples with residual methoxy on the surface to yield methyl formate. Exposure of the titania surface to O_2 is required for these photo-oxidation steps in order to heal surface and near-surface defects that can serve as hole traps. Notably, residual O adatoms are *not* required for photochemical production of methyl formate or formaldehyde. All O adatoms react thermally with methanol to form methoxy and gaseous water at rt, leaving a surface devoid of O adatoms. The mechanism provides insight into the photochemistry of TiO_2 and suggests general synthetic pathways that are the result of the ability to activate both alkoxides and aldehydes using photons.

Titanium dioxide has been studied widely as a promising photocatalyst for green chemistry.[1−3] The photochemistry of methanol on TiO_2 in particular has been studied under a variety of conditions because it facilitates water splitting on titania.[1,4−7] Even so, discrepancies and unanswered questions remain about the photo-oxidation of methanol. For example, on reduced $TiO_2(110)$, UV light is proposed to induce formation of methoxy from methanol.[7] Alternatively, O adatoms can be used to thermally dissociate methanol into methoxy on $TiO_2(110)$.[1] Methoxy is proposed to be the photoactive species for production of formaldehyde on TiO_2, not molecular methanol.[5] It loses a H photolytically to yield formaldehyde, proposed to be due to the photochemical production of holes on bridging O which abstract the H.[5]

While formaldehyde is clearly formed as an initial photo-oxidation product from methoxy on TiO_2,[5−7] we observe the production of both formaldehyde and methyl formate. Indeed, methyl formate has also been reported in recent gas-phase studies of the photochemical reactions of methanol over anatase particles.[8]

In this work, we investigate the photo-oxidation of methanol on rutile $TiO_2(110)$ to yield both formaldehyde and methyl formate. We demonstrate that methyl formate production occurs via the mechanism described in Scheme 1, with two sequential photochemical steps following the initial thermal activation of methanol by O adatoms to quantitatively yield methoxy.[5,9] Oxygen adatoms thermally drive the first step, creating a photoactive methoxy, whereas bridging oxygen facilitates the removal of hydrogen in the light-induced steps[5] because the adatoms have reacted away. Titania photochemistry is generally hole-mediated because the hole is localized at the surface.[2]

Scheme 1. Mechanism of the Oxidation of Methanol to Methyl Formate



The photo-oxidation of methanol to both formaldeyde and methyl formate via UV photolysis of methoxy on $TiO_2(110)$ is clearly demonstrated by the evolution of both products in the comparison of temperature programmed data before and after photolysis at 200 K (Figure 1A). In the absence of UV irradiation, molecular methanol desorbs at ~280 K and methoxy disproportionates to formaldehyde and methanol at ~670 K, in agreement with previous work.[1,5,7] No methyl formate is detected during heating (Figure 1A). Following illumination with UV light, formaldehyde and methyl formate desorb at ~250 and ~260 K, respectively, and there are no products at higher temperatures that would be characteristic of methoxy (Figure 1A). These results establish that methoxy is completely converted to $H_2C{=}O$ and $HCOOCH_3$ via photo-oxidation.

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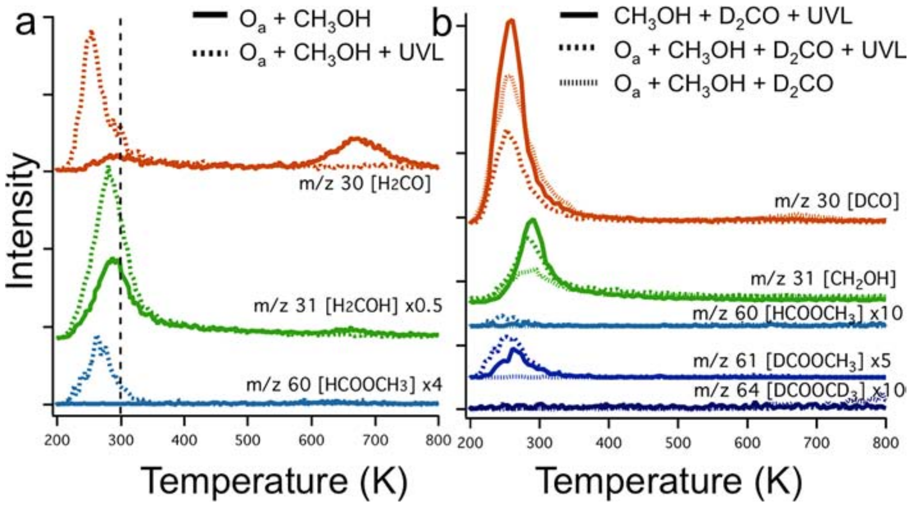

Figure 1. Temperature programmed reaction experiments of methanol oxidation to methyl formate (a) and photochemical coupling with d_2-formaldehyde (b). In (a), data are shown after exposure of the surface to methanol (solid line) and after 300 s of illumination with UV light at 200 K (dashed line). In (b), data are shown for the reduced (solid line) and preoxidized (dashed and dotted lines) surface, followed by 300 s of illumination (solid and dashed lines). For all experiments, oxygen adatoms are produced by exposure to O_2 (200 L) on the as-prepared $TiO_2(110)$ surface at 300 K. The surface was then cooled to 200 K for methanol or methanol and then formaldehyde adsorption (~0.3 ML), followed by illumination for 300 s with a Xe arc lamp with a short-pass filter allowing 200−400 nm light through. A constant 2 K/s heating rate was used. In sets of data, the contributions to *m*/*z* 30 and 31 from methyl formate and the contribution to *m*/*z* 30 from methanol were subtracted.

We established the two-step photochemical mechanism by demonstrating that UV light is required to produce methyl formate even when formaldehyde is coadsorbed with methoxy. Illumination of adsorbed methanol followed by d_2-formaldehyde yields $DCOOCH_3$ (*m*/*z* 61) in temperature programmed experiments (Figure 1B, solid and dashed lines). No $DCOOCD_3$ (*m*/*z* 64) is detected in any of the experiments, demonstrating that intact methoxy is required for methyl formate production. The methoxy coupling product, $HCOOCH_3$ (*m*/*z* 60), is only found when the surface is first oxidized and subsequently illuminated with UV light, and the yield is much smaller than $DCOOCH_3$ (Figure 1B). This indicates that the methanol is still reacting with itself to some extent. Since no methyl formate is produced without photolysis even when $D_2C{=}O$ is present, it is clear that a second photolytic step is still required for methyl formate production. Desorption of unreacted methanol and formaldehyde is also observed. These experiments establish that (1) methyl formate is produced from coupling of methoxy with a product of formaldehyde; (2) photo-oxidation of formaldehyde by UV light is required to produce methyl formate; and (3) exposure of the surface to oxygen increases the yield of methyl formate by promoting methoxy formation.

Several control experiments rule out two possible mechanisms. First, no methyl formate is produced either thermally or photolytically from formaldehyde alone (data not shown), ruling out formaldehyde coupling and rearrangement by the so-called Tishchenko mechanism.[10] Additionally, no methyl formate is produced in a temperature programmed reaction when coadsorbed methanol and formate are illuminated with UV light (Figure S1), ruling out formate as the intermediate.

Formaldehyde and methyl formate evolution into the gas phase during UV irradiation is also observed (Figure 2). Formaldehyde is evolved into the gas phase during photolysis at surface temperatures of both 200 and 300 K, indicating that formaldehyde is a primary photoproduct. In contrast, methyl formate is only detected in the gas phase during photolysis at 300 K (Figure 2). These data are evidence that methyl formate is trapped on the surface after it is formed at 200 K and that its evolution into the gas phase is limited by desorption from the surface. Production of methyl formate requires that both methoxy and formaldehyde be present on the surface, indicating that the photochemical activation of formaldehyde is faster than the methoxy photo-oxidation to formaldehyde. The complexity of the overall process precludes a quantitative kinetic analysis; more details are discussed in section 5 of the Supporting Information.

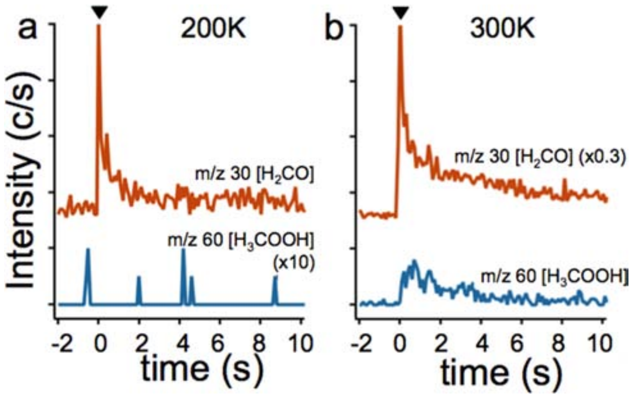

Figure 2. Photon-stimulated production of formaldehyde (*m*/*z* 30) and methyl formate (*m*/*z* 60) from methanol and O adatoms on TiO_2 (110) were monitored using mass spectrometry at two different temperatures, (a) 200 K and (b) 300 K. Oxygen adatoms are produced on the surface by exposure to O_2 (200 L) on the as-prepared TiO_2 (110) surface at 300 K. In (a), the surface was then cooled to 200 K for methanol adsorption, followed by illumination. A Xe arc lamp with a short-pass filter was used as the light source (92 mW/cm^2 total flux). The total photolysis time was 300 s; only the first 10 s are shown for clarity.

Scanning tunneling microscopy (STM) images provide supporting evidence that methyl formate, produced at low temperature in the photo-oxidation of methanol on TiO_2, is trapped on the surface first, followed by desorption at ~260 K

(Figure 3). At rt, illumination of methoxy results in a surface that is essentially clean, a result consistent with the fact that both formaldehyde and methyl formate desorb below 300 K (Figure S2). At 50 K, however, the photoproduct is trapped on the surface, showing that two methoxy species present before illumination are converted to a single larger feature, attributed to methyl formate, after exposure to UV light (Figure 3a,b). The tip was retracted 1 cm during illumination, and the same terrace was found afterward to image. Indeed, the features of the photoproduct are identical in length and apparent height to the images obtained for methyl formate adsorbed on as-prepared $TiO_2(110)$ (Figure 3c,d). These data also suggest that the proximity of two methoxy species during photo-oxidation may facilitate the coupling process.

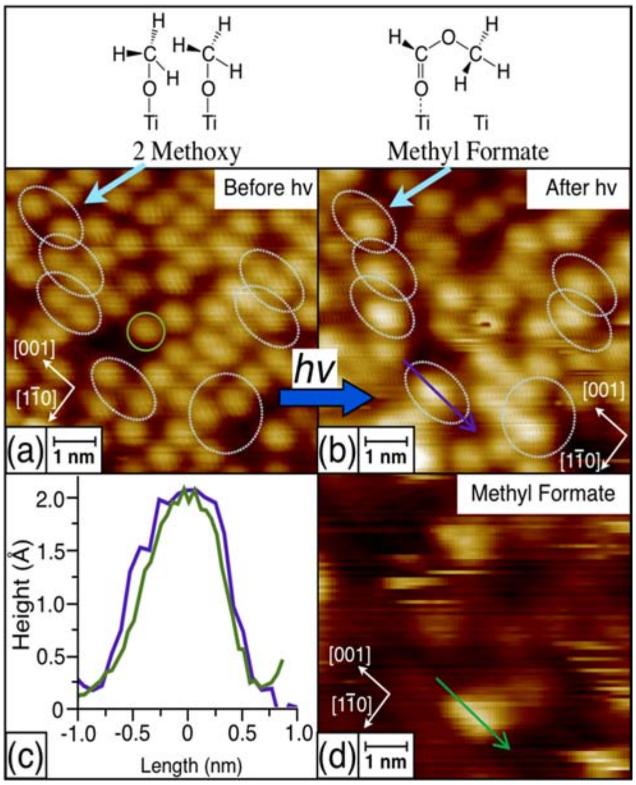

Figure 3. Photolysis of methoxy groups on o-TiO_2 (110) at 50 K create new features that match methyl formate. (a) Methoxy created by depositing 300 L of O_2 at 300 K followed by saturation coverage of methanol at 300 K and warming to 340 K to desorb molecularly adsorbed methanol before cooling to 50 K for imaging. Each circular feature is a methoxy. (One such feature is circled in green.) Pairs circled with a dotted line couple to form methyl formate after UV illumination (I_t = 0.08 nA; V_s = +1.3 V). (b) Same area as (a) after 5 min of UV illumination. Circled features are newly created from the combination of two methoxy features (I_t = 0.08 nA; V_s = +0.74 V). (c) Comparison of the apparent feature heights of a new feature created in (b) (in purple) to methyl formate deposited in a separate experiment on r-TiO_2 (110) shown in (d) (in green). Both features are essentially identical in both height and length along the Ti rows. (d) Low coverage of methyl formate deposited on the as prepared TiO_2 (110) surface at 70 K. UV photon illumination was performed with a Xe lamp with a bandwidth of 200−400 nm (92 mw/cm^2 total flux). The higher imaging temperature and the low coverage slightly degrade the image quality for adsorbed methyl formate.

We propose that a transient formyl (HCO) is produced in the secondary photo-oxidation of formaldehyde. Evidence for the production of transient HCO is derived from results showing that formate is produced by UV irradiation of formaldehyde adsorbed on $TiO_2(110)$ containing O adatoms. Transient HCO produced from $H_2C{=}O$ photo-oxidation would readily add to O adatoms on titania to produce the stable formate species. Our evidence for the production of formate is the signature production of CO_2 at 570 K in temperature programmed experiments performed following UV illumination of formaldehyde in the presence of O adatoms (Figure S3). In the absence of O adatoms, HCO can react with methoxy to produce methyl formate.

The production of HCO from photo-oxidation of formaldehyde is a reasonable pathway based on known gas-phase photochemistry. First, exposure of gaseous formaldehyde to 334 nm light forms HCO,[11] although a mechanism involving the direct excitation of formaldehyde is unlikely due to its extremely low absorption cross section in the UV ($\sim 10^{-19}$ cm^2).[12] Methyl formate itself decomposes to HCO and CH_3O by a Norrish Type I reaction in the gas phase, demonstrating that CH_3O and HCO correlate to an excited state of methyl formate.[13]

The photoproduct methyl formate has been seen previously on anatase nanoparticles in a flow reactor,[8] but our finding extends the range of reaction conditions for which the self-coupling occurs to lower pressure and to rutile TiO_2. Formaldehyde is found as a minor product in ambient catalysis on titania nanoparticles as well,[8] so they propose formaldehyde dimerization, or the Tishchenko mechanism,[10] as the pathway. Our results indicate that it is instead a formyl intermediate. We specifically rule out the Tishenko mechanism based on the lack of formaldehyde coupling (Figure 1b).

Several other studies did not report the product, including both rutile and mixed-phase ambient pressure studies.[14−16] Although methyl formate production was not reported in previous ultrahigh vacuum studies of methanol photo-oxidation on $TiO_2(110)$,[4−6] methyl formate was probably produced, but not detected. In previous work, m/z 29 was used to identify formaldehyde. While this ion is a major fragment of formaldehyde, it is also a common ion for other organic oxygenates, including methyl formate. In more recent studies focusing on formaldehyde production, a comment is made about the formation of methyl formate without supporting data.[7]

The photo-oxidation of methoxy to formaldehyde and methyl formate provide evidence that an important role of oxygen in these processes is to eliminate trap states that lead to rapid (~femtoseconds) electron−hole pair recombination. A time-dependent two-photon photoemission study on the reduced surface found evidence for two sequential photochemical steps, but they did not report any methyl formate,[4] consistent with our work. Parallel STM experiments did not provide evidence for methyl formate either, although the coverage of reactants was low (0.02 monolayer).[4]

Previous studies of the photo-oxidation of methoxy to formaldehyde demonstrate that the hydrogen abstracted in the process resides on a bridging oxygen.[5] These results suggest that bridging O is the photoactive species, pulling off the hydrogen from methoxy. Even if methoxy reacts with an exciton created in the TiO_2 bulk, oxygen exposure quenches recombination by coordination to bridging oxygen vacancies and Ti interstitials.[3]

By analogy, we also propose that the hydrogen abstracted from formaldehyde is transferred to bridging O. The production of HCO from formaldehyde is similar to the abstraction of H from CH_3O;[5] therefore, we similarly propose that a hole created on bridging O from UV excitation drives the photo-oxidation of formaldehyde. DFT calculations show formaldehyde tilted toward bridging oxygen,[17] which could facilitate H abstraction.

Our work demonstrates that it is not necessary to have O adatoms on the surface for the photochemical activity of TiO_2(110). In our studies, there are no residual O adatoms on the surface because they quantitatively react with methanol and are removed as water,[6] although the vacancies are still filled. Thus, while exposure to O_2 is critical to limit charge carrier recombination by filling vacancies,[3] residual O adatoms are *not* necessary for photo-oxidation. If residual O adatoms were present, they would trap the product of formaldehyde photo-oxidation, HCO, as formate and inhibit production of methyl formate.

The mechanism determined in this work provides insights into the design of photosynthetic processes on titania. The fact that methyl formate is produced suggests that formaldehyde photo-oxidation occurs on a somewhat faster time scale than methoxy. This observation suggests that rapid photo-oxidation of aldehydes might be a versatile means of producing extremely reactive intermediates on the surface that could drive other photosynthetic processes, creating a new class of photocatalytic reactions on TiO_2. More detailed analysis of the time scales for the various steps using ultrafast laser techniques would help guide the experimental design of such photosynthetic pathways.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, formic acid−methanol coadsorption results, STM images showing the surface cleaning off upon illumination, and results showing formaldehyde reacting to form formate upon illumination. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interests.

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