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Molecular Hydrogen Formation from Photocatalysis of Methanol on Anatase-TiO_2(101)

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Supporting Information

ABSTRACT: Photocatalysis of methanol (CH_3OH) on anatase (A)-TiO_2(101) has been investigated using temperature programmed desorption (TPD) method with 266 nm light at low surface temperatures. Experimental results show that CH_3OH adsorbs on the A-TiO_2(101) surface predominantly in molecular form, with only a small amount of CH_3OH in dissociated form. Photocatalytic products, formaldehyde (CH_2O) and methyl formate ($HCOOCH_3$), have been detected under 266 nm light irradiation. In addition to H_2O formation, H_2 product is also observed by TPD spectroscopy. Experimental results indicate that H_2 product is formed via thermal recombination of H-atoms on the BBO sites from photocatalysis of CH_3OH on the A-TiO_2(101) surface, and H_2 production on the A-TiO_2(101) surface is significantly more efficient than that on the rutile (R)-TiO_2(110) surface.

Titanium dioxide, TiO_2, is a widely used material with important applications in many areas, particularly in heterogeneous catalysis, gas sensors, and electronic devices and biomaterials.[1−8] TiO_2 exists in three polymorphs: rutile, anatase, and brookite. Rutile and anatase TiO_2 materials have been often used in the study of hydrogen (H_2) production from photocatalytic water splitting,[9−11] as well as degradation of organic pollutants.[12] Despite lots of work focusing on rutile (R)-TiO_2, the anatase form is the most active polymorph in commercial applications for catalysis actually.[5] A previous study found that adding methanol (CH_3OH) to pure water solution can dramatically enhance H_2 production, implying that CH_3OH played a crucial role in H_2 production.[13] In recent years, photocatalysis of CH_3OH on TiO_2 has been extensively studied as a benchmark system.[2,14−23] Elementary processes in CH_3OH photocatalysis on the R-TiO_2(110) surface have been clarified. Most recently,[24] we have shown that D_2 can be formed via thermal recombination of dissociated D-atoms on the bridge-bonded oxygen (BBO) sites from photocatalysis of fully deuterated CH_3OH, suggesting that the last molecular D_2 formation step on the R-TiO_2(110) surface is a thermally driven process. Since only about 7% of D-atoms on the BBO sites contribute to D_2 formation with most D-atoms recombining with BBO atoms to form D_2O, it implies that H_2 formation is not the most efficient process on the R-TiO_2(110) surface. Even though a lot of photocatslysis studies have been carried out on anatase (A)-TiO_2 particles, very little was done on well-defined surfaces. Thus far, only a few experimental studies of thermal chemistry on A-TiO_2(101) have been carried out,[25−30] and photocatalytic chemistry on this well-defined surface has not been investigated at all. In this work, we have investigated molecular H_2 formation on A-TiO_2(101) from photocatalysis of CH_3OH using temperature programmed desorption (TPD) and time-of-flight (TOF) methods, in combination with laser surface photocatalysis. Our results show that H_2 is formed via thermal recombination of dissociated H-atoms on the BBO sites from photocatalysis of CH_3OH on A-TiO_2(101). In addition, we found that H_2 formation on A-TiO_2(101) is considerably more efficient that on R-TiO_2(110).[24]

The surface photocatalysis-TPD apparatus used in this work has been described previously in detail.[22,31] The base pressure of the sample chamber is $<6 \times 10^{-11}$ Torr. A highly sensitive quadrupole mass spectrometer (QMS) (Extrel) is used to detect TPD and TOF products from the surface. An extremely high vacuum of 1.5×10^{-12} Torr was achieved and maintained in the electron-impact ionization region. The A-TiO_2(101) (6×1 mm^3, Princeton Scientific Corp.) surface was prepared by cycles of Ar^+ sputtering and resistive heating to 800 K in vacuum until all impurities were removed. CH_3OH (Aldrich, 99.9%) purified by several freeze/pump/thaw cycles was introduced to the A-TiO_2(101) surface with a calibrated molecular beam doser. The 266 nm light used to irradiate the TiO_2 surface came from a frequency tripled Ti:Sapphire femtosecond laser (repetition rate 1 kHz, pulse duration ~70 fs). About a 20 mW laser light beam with a diameter of 3 mm was directed at the sample surface at an angle of ~30° from the surface parallel. The photo flux impinging on the surface is 1.9×10^{17} photons cm^{-2} s^{-1}. The TPD spectrum after a certain time of laser irradiation was measured with a heating rate of 2 K/s, with the surface directly pointing to the mass spectrometer. In addition, TOF measurements for certain photodesorbed products were also made during laser irradiation.

Before investigating the photocatalytic chemistry of CH_3OH, TPD spectra of CH_3OH on the A-TiO_2(101) surface as a function of coverage were measured (Supporting Information (SI) Figure S1). Five desorption features peaked at 142 K, 188 K, 270 K, 410 K, and 650 K are observed, similar to previous results with slightly better resolution.[29] A 650 K peak is also observed in TPD spectra at m/z = 30, 31, and 32 (SI Figure S2). This is likely

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due to methoxy (CH_3O) disproportionation at the five-coordinated Ti^{4+}(Ti_{5c}) sites, as on the R-TiO_2(110) surface,[21]

$$CH_3OH(Ti_{5c}) \xrightarrow{A-TiO_2(101)} CH_3O(Ti_{5c}) + H-O_{BBO} \quad (1)$$

$$2CH_3O(Ti_{5c}) \xrightarrow{heat,A-TiO_2(101)} CH_3OH(gas) + CH_2O(gas) \quad (2)$$

where O_{BBO} is bridge bonded oxygen and the coverage of $CH_3O(Ti_{5c})$ from m/z = 30 and 31 TPD is calculated to about 0.02 ML. The fact that the 650 K peak in m/z = 30 and 31 TPD decreases rapidly after 5 s of irradiation while the 300 K peak changes little implies that CH_3O has a much higher reactivity than molecular CH_3OH on this surface (Figure 1A and B). This is consistent with previous studies by Shen and Henderson on R-TiO_2(110).[21]

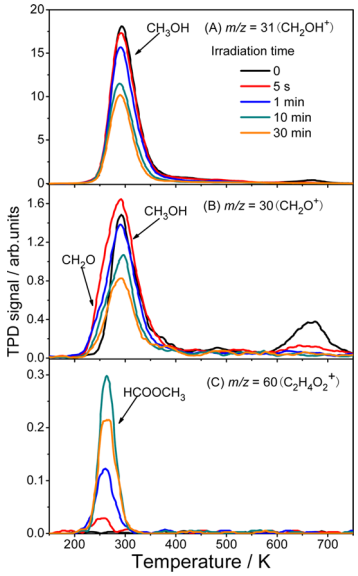

Figure 1. 0.38 ML of CH_3OH were dosed to the A-TiO_2(101) surfaces at 100 K. (A) Typical TPD spectra collected at m/z = 31 (CH_2OH^+) as a function of irradiation time with a photon flux of 1.9 × 10^{17} photons cm^{-2} s^{-1}. CH_2OH^+ is mainly formed by dissociative ionization of the desorbed parent CH_3OH molecule in the electron-bombardment ionizer. (B) Typical TPD spectra collected at m/z = 30 (CH_2O^+) as a function of irradiation time. The m/z = 30 (CH_2O^+) signal has two components: the parent ion signal of formaldehyde (CH_2O), as well as the ion-fragment signals of the parent CH_3OH molecule. (C) Typical TPD spectra collected at m/z = 60 ($C_2H_4O_2^+$) as a function of irradiation time. The m/z = 60 ($C_2H_4O_2^+$) signal is from the parent ion signal of $HCOOCH_3$ molecule.

We then carried out a systematic study on the photocatalytic chemistry of 0.38 ML of CH_3OH covered A-TiO_2(110) surface using 266 nm light with different irradiation times. As shown in Figure 1A, the 290 K peak at TPD spectra of m/z = 31 (CH_2OH^+), which is assigned to molecular CH_3OH desorption from Ti_{5c} sites, decreases as irradiation time increasing, suggesting that CH_3OH on the A-TiO_2(101) surface has been photocatalytically dissociated. Photocatalytic products, formaldehyde (CH_2O at m/z = 30) and methyl formate ($HCOOCH_3$ at m/z = 60), have been clearly detected with different laser irradiation times (Figure 1B and C). Meanwhile, TOF signals of CH_2O (m/z = 30) and CH_3OH (m/z = 32) were monitored during laser irradiation (SI Figure S3). The intensity of the TOF signal at m/z = 30 is about 4 times larger than that at m/z = 32, and whereas the cracking signal of CH_3OH to m/z = 30 is only $^1/_5$ of the parent mass ion signal in our quadrupole mass detector (SI Figure S4), the fact that the TOF signal at m/z = 30 is considerably larger implies that the TOF signal at m/z = 30 should mostly come from photodesorbed CH_2O on Ti_{5c} sites. These observed products are similar to that on the R-TiO_2(110) surface.[32] The photocatalytic mechanisms for the formation of these products are also believed to be similar to that on the R-TiO_2(110) surface. The most likely mechanism of CH_2O formation is via transferring the hydroxyl H and a methyl group H of CH_3OH to the O_{BBO} sites nearby, while the product $HCOOCH_3$ is likely formed through a cross coupling reaction of CH_2O and CH_3O, similar to that on the R-TiO_2(110) surface.[32] The formation of $HCOOCH_3$ is an indirect evidence of the existence of $CH_3O(Ti_{5c})$.

$$CH_3OH(Ti_{5c}) \xrightarrow{h\nu,A-TiO_2(101)} CH_3O(Ti_{5c}) + H-O_{BBO} \quad (3)$$

$$CH_3O(Ti_{5c}) \xrightarrow{h\nu,A-TiO_2(101)} CH_2O(Ti_{5c}) + H-O_{BBO} \quad (4)$$

$$CH_3O(Ti_{5c}) + CH_2O(Ti_{5c}) \xrightarrow{h\nu,A-TiO_2(101)} HCOOOCH_3(Ti_{5c}) + H-O_{BBO} \quad (5)$$

In these processes, dissociated H atoms are transferred to the O_{BBO} sites. It is thus interesting to see how molecular H_2 is formed from these dissociated H atoms.

To detect dissociated H-atoms from photocatalysis of CH_3OH on the A-TiO_2(101) surface, we have measured TPD spectra at different masses. Figure 2A shows TPD spectra at m/z = 18

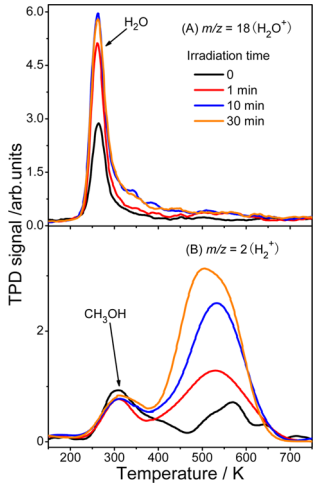

Figure 2. TPD spectra collected at m/z = 2 and 18, from photocatalysis of 0.38 ML of CH_3OH covered A-TiO_2(101) at 100 K with a photon flux of 1.9 × 10^{17} photons cm^{-2} s^{-1}.

(H_2O^+) after different irradiation durations with 0.38 ML of CH_3OH covered A-TiO_2(101) surface. Before irradiation, a rather sharp peak at m/z = 18 is observed near 260 K. This is assigned to H_2O desorption from Ti_{5c} sites. No obvious H_2O desorption signal was detected at higher temperature, suggesting that there are nearly no point defects on the surface. A recent study shows that only about 0.005 ML of point defects on the A-TiO_2(101) surface could be formed by annealing.[33] However, the amount of desorbed H_2O observed here corresponds to about 0.025 ML, which is about 6.6% of all CH_3OH adsorbed on

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the surface. This could not be attributed to the impurity of H_2O in the CH_3OH sample, which is <0.6%, according to our measurement on the R-TiO_2(110) surface using the same CH_3OH sample. Thus, the desorbed H_2O at 260 K must come from some thermal reactions during the TPD process. In addition, a broad TPD peak from 400 to 700 K was also detected at m/z = 15 (SI Figure S5). The direct desorption of CH_3 radical could be related to the H_2O TPD desorption at 260 K. From these results, we propose that the H_2O TPD peak at 260 K is due to the following thermally driven exchange reaction (Figure 3):

$$CH_3OH(Ti_{5c}) + H{-}O_{BBO} \xrightarrow{heat,A{-}TiO_2(101)} CH_3{-}O_{BBO} + H_2O(Ti_{5c}) \quad (6)$$

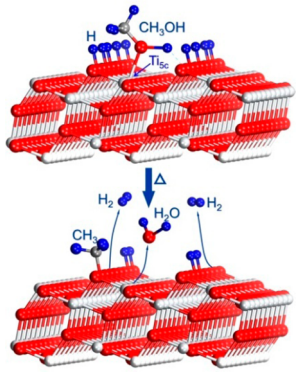

Figure 3. Schematic diagram of the mechanism of molecular H_2 production from $H{-}O_{BBO}$ on a A-TiO_2(101) surface.

This is similar to previous experimental observations.[34] The original HO_{BBO} species here should come from the small amount of dissociatively adsorbed CH_3OH on the surface. Furthermore, the TOF signal of CH_3 (SI Figure S3) from likely $CH_3{-}O_{BBO}$ was also detected, consistent with the above picture. As more $H{-}O_{BBO}$ species are formed from photocatalysis of CH_3OH on the A-TiO_2(101) surface, the H_2O TPD peak increases (Figure 2A). The intensity of the H_2O TPD peak reaches a maximum after 10 min of laser irradiation. However, the photoinduced H_2O signal is only slightly larger than that without laser irradiation, suggesting that the H_2O formation process is not enhanced significantly by photocatalysis.

As shown above, some $H{-}O_{BBO}$ species are depleted by exchanging with CH_3 groups in CH_3OH so that H_2O will be formed. Molecular H_2 may be formed by recombination of $H{-}O_{BBO}$ as in the case of R-TiO_2(110).[24] It is thus interesting to know the relative importance of molecular H_2 formation versus H_2O formation on the A-TiO_2(101) surface, since this could relate to the efficiency of H_2 production. In the case of CD_3OD photocatalysis on the R-TiO_2(110) surface, D_2O formation is much more important than D_2 formation (see SI Figure S6), suggesting that H_2 formation is less efficient. Indeed, when we have attempted to detect H_2 product from photocatalysis of CH_3OH on R-TiO_2(110), no signal was detected.

To determine if molecular H_2 product could be formed, TPD spectra at m/z = 2 (H_2^+) were measured after 266 nm laser irradiation, as shown in Figure 2B. There are two main sources of signals at m/z = 2. Clearly, the TPD peak at about 300 K comes from the fragmentation of desorbed molecular CH_3OH in the ionizer. Another obvious source is the H_2 product formed via recombinative desorption of $H{-}O_{BBO}$. As indicated in Figure 2B, the TPD peak near 550 K is most likely due to this source and is strongly dependent on the laser irradiation time. When the surface temperature is above 400 K, CH_2O, CH_3OH, $HCOOCH_3$, and H_2O on A-TiO_2(101) have all been desorbed, and CH_3O_{BBO}, HO_{BBO}, and $CH_3O(Ti^{4+})$ are the only three species left. Obviously, $CH_3O(Ti^{4+})$ is mostly depleted after laser irradiation for only 1 min. No evidence of any other larger molecules on the surface is observed during TPD measurements. The contribution of the fragmentation from CH_3 radical at m/z = 2 is quite small before irradiation. After 30 min irradiation, the intensity of the CH_3 radical peak only increases by about 2 times (SI Figure S5). Thus, we can conclude that the 550 K TPD desorption peak at m/z = 2 arises mainly from the recombination of H atoms at O_{BBO} sites (Figure 3):

$$2H{-}O_{BBO} \xrightarrow{heat,A{-}TiO_2(101)} H_2(gas) + 2O_{BBO} \quad (7)$$

We have also attempted to detect H_2 product during laser irradiation and no signal was detected, indicating that H_2 formation is a thermally driven recombination process, not a photodriven reaction. From the above results and our previous studies,[24] it is clear that molecular H_2 formation from photocatalysis of CH_3OH on A-TiO_2(101) occurs via photocatalytic dissociation of CH_3OH followed by thermal recombination of $H{-}O_{BBO}$, similar to that on R-TiO_2(110).

We now evaluate the relative importance of H_2 formation in comparison to H_2O formation on A-TiO_2(101). To do that, the yields of H_2O and H_2 products as a function of laser irradiation time have been measured and plotted in Figure 4. The yields of

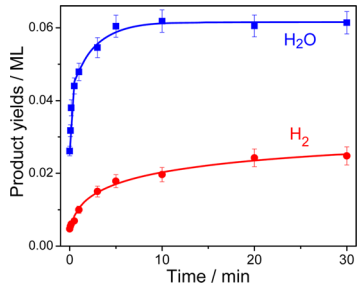

Figure 4. Yields of the molecular H_2, H_2O TPD products as a function of laser irradiation time.

H_2O and H_2 products shown in Figure 4 have already been calibrated based on the detection efficiencies of the two products in the quadrupole mass detector. The result of the current measurement shows that 0.025 ML of H_2 and 0.035 ML of H_2O are formed after 30 min of irradiation. This indicates that the H_2 formation channel is nearly as important as the H_2O formation process on the A-TiO_2(101) surface. This result is significantly different from that on the R-TiO_2(110) surface. On the R-TiO_2(110) surface, we have shown than the D_2O formation process is about 13 times more efficient than the molecular D_2 formation process.[24] It is interesting to note that the H_2O TPD signal reaches maximum at 10 min while the H_2 TPD signal continues to grow up at 30 min on the A-TiO_2(101) surface. In addition, the H_2O formation mechanisms are also quite different for the two surfaces. We have attempted to measure the TOF signal of O-atom from a bare A-TiO_2(101) surface when irradiated with UV light, and no measurable O-atom TOF signal was detected, suggesting that no surface defects are created during UV irradiation and the O_{BBO} atoms are very stable. This is likely the reason that dissociated H atoms at the O_{BBO} sites

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mostly come off as H_2 on the A-TiO_2(101) surface, not taking an O_{BBO} to form H_2O (Figure 3). Thus, if there is the same amount of H-atoms on the BBO sites, molecular H_2 formation on the A-TiO_2(101) surface should be more efficient than that on the R-TiO_2(110) surface.

In present study, relatively monochromatic UV light is used to study photoctalysis on a well characterized surface in ultrahigh vacuum, while most photocatalysis studies use particle photocatalysts under bulk conditions and discharge lamps that also contain UV light. The purpose of the current study is to try to understand the underlying elementary photocatalytic processes, which are difficult to probe in bulk experiments.

UV photocatalysis of CH_3OH on a well-defined A-TiO_2(101) surface has been investigated using TPD and TOF methods. Experimental results show unambiguously that molecular H_2 formation from UV photocatalysis of CH_3OH on the A-TiO_2(101) surface is a thermally driven process that occurs via H-atom recombination on the O_{BBO} sites and is clearly not a photodriven process. More interestingly, we found that formation of molecular H_2 and H_2O are comparable on the A-TiO_2(101) surface, while formation of molecular H_2 on R-TiO_2(110) is much less efficient than H_2O. This suggests that the H_2 formation process should be more efficient on the A-TiO_2(101) surface relative to the R-TiO_2(110) surface. The present investigation of the mechanism of H_2 formation from UV methanol photocatalysis on A-TiO_2(101) could also help us to understand the nature of H_2 production on TiO_2 photocatalysts.

■ ASSOCIATED CONTENT

Supporting Information

Yield and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

[§]C.X. and W.Y. made similar contributions to this work.

Notes

The authors declare no competing financial interest.

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