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Molecular Hydrogen Formation from Photocatalysis of Methanol on $TiO_2(110)$

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S *Supporting Information*

ABSTRACT: It is well established that adding methanol to water could significantly enhance H_2 production by TiO_2. Recently, we have found that methanol can be photocatalytically dissociated on $TiO_2(110)$ at 400 nm via a stepwise mechanism. However, how molecular hydrogen can be formed from the photocatalyzed methanol/$TiO_2(110)$ surface is still not clear. In this work, we have investigated deuterium formation from photocatalysis of the fully deuterated methanol (CD_3OD) on $TiO_2(110)$ at 400 nm using a temperature programmed desorption (TPD) technique. Photocatalytic dissociation products formaldehyde (CD_2O) and D-atoms on BBO sites (via D_2O TPD product) have been detected. In addition to D_2O formation by heating the photocatalyzed methanol/$TiO_2(110)$ surface, we have also observed D_2 product formation. D_2 is clearly formed via thermal recombination of the D-atoms on the BBO sites from photocatalysis of methanol. Experimental results indicate that D_2O formation is more important than D_2 formation and that D_2 formation is clearly affected by the D_2O formation process.

TiO_2 has attracted enormous interest in heterogeneous catalysis, photocatalysis, solar energy devices, etc.[1−8] Photocatalytic water splitting by TiO_2 is especially attractive because of its potential application in clean hydrogen production.[9] A previous study found that pure TiO_2 is not active for hydrogen production from pure water.[10] Adding methanol to pure water, however, can dramatically enhance hydrogen production.[11] Because of the apparently crucial role in hydrogen production, the photochemistry of methanol has been extensively investigated on single crystal TiO_2 surfaces[12−31] and TiO_2 powders.[32−35] Although investigations on powder TiO_2 with methanol steam[32−35] and a water−methanol mixture[11] show that hydrogen can be produced from methanol by reaction,

$$CH_3OH \xrightarrow{h\nu + heat,\ TiO_2} CH_2O + H_2 \qquad (1)$$

the detailed mechanism of gaseous hydrogen formation from methanol photocatalysis on TiO_2 remains unknown. In a recent study,[28] we have shown that the elementary photocatalytic dissociation of CH_3OH on $TiO_2(110)$ without any other coadsorbed species occurs in a stepwise mechanism in which the O−H dissociation proceeds first and is then followed by C−H dissociation to form formaldehyde (CH_2O) with only methanol adsorption on $TiO_2(110)$,

$$CH_3OH(Ti_{5C}) \xrightarrow{h\nu, TiO_2(110)} CH_3O(Ti_{5C}) + H_{BBO} \qquad (2)$$

$$CH_3O(Ti_{5C}) \xrightarrow{h\nu, TiO_2(110)} CH_2O(Ti_{5C}) + H_{BBO} \qquad (3)$$

where Ti_{5C} refers to a five-coordinated $Ti^{4+}(Ti_{5C})$ site, and H_{BBO} refers to an H atom adsorbed on a bridge-bonded oxygen (BBO) site on the $TiO_2(110)$ surface. From our experiment, we have found that both dissociation steps are photoinitiated. This means that at low temperature photocatalytic dissociation products from CH_3OH, i.e., CH_2O and H atoms on BBO sites, are all left on the TiO_2 surface after laser irradiation, whereas Henderson and co-workers found that molecular CH_3OH is not photoactive on $TiO_2(110)$ using a Hg lamp as the surface photocatalysis source.[26] In our experiment,[28,36] we used a femtosecond laser source that has considerably higher photon flux than the Hg lamp used in ref 26, in addition to the highly sensitive mass spectrometric detector with a vacuum background of 1×10^{-12} Torr. We believe this makes our experiment much more sensitive in detecting TPD products. Further oxidation of CH_3OH on $TiO_2(110)$ to form methyl formate has also been observed in three different laboratories.[36−38] However, the important question of how hydrogen molecules are formed from the photocatalysis of methanol on $TiO_2(110)$ remains unanswered.

In order to understand the mechanism of hydrogen formation, the photocatalytic chemistry of CD_3OD has been investigated on the $TiO_2(110)$ surface using temperature programmed desorption (TPD), in combination with laser surface photocatalysis. The surface photocatalysis-TPD apparatus used in this work has been described previously in detail.[28,39] The base pressure of the sample chamber of this apparatus is less than 6×10^{-11} Torr. A highly sensitive quadrupole mass spectrometer (Extrel) is used to detect TPD products. To achieve the highest detection sensitivity and the lowest background, an extremely high vacuum of 1.5×10^{-12} Torr was achieved and maintained in the electron-impact ionization region during the experiments for sensitive product detection. The $TiO_2(110)$ surface was cleaned by cycles of Ar^+ sputtering and resistive heating to 850 K in a vacuum until all impurities were removed. The $TiO_2(110)$ surface contained 3−

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4% O-vacancy defects as determined by H_2O TPD.[40] CD_3OD (Aldrich, 99+%) was purified by several freeze−pump−thaw cycles and was introduced onto the $TiO_2(110)$ surface with an accurately calibrated molecular beam doser. The surface temperature was maintained at 120 K during CD_3OD sample dosing, and it typically rose to ∼180 K during laser irradiation. The 400 nm irradiating light came from a frequency doubled Ti:Sapphire femtosecond laser (repetition rate 1 kHz). The average intensity of the laser beam on the sample was 400 mW with a diameter of 6 mm, corresponding to a flux of $\sim 1.44 \times 10^{18}$ photons cm^{-2} s^{-1}. The light was incident on the $TiO_2(110)$ at ∼30° with respect to the $TiO_2(110)$ surface. TPD spectra after laser irradiation were measured using a heating rate of 2 K/s, with the surface normal directly pointing to the mass spectrometer.

The first experiment we carried out in this work was the investigation of the photocatalytic dissociation of CD_3OD by measuring the TPD spectra of the CD_3OD reactant (Figure S1A) and CD_2O product (Figure S1B) as a function of 400 nm laser irradiation time. The TPD spectra at $m/z = 36$ (CD_3OD^+) and $m/z = 32$ (CD_2O^+) show that CD_3OD becomes photocatalytically dissociated, while CD_2O is formed. This result is analogous to our earlier observations involving CD_3OH[28] and CH_3OH[36] on $TiO_2(110)$. In order to detect D-atoms on the BBO rows from the photocatalytic dissociation of CD_3OD on $TiO_2(110)$, TPD spectra (Figure 1A) at $m/z = 20$ (D_2O^+) have been measured, after different irradiation durations following adsorption of 0.5 ML of CD_3OD on $TiO_2(110)$. Two main features are observed in the TPD spectra. The peak (marked with *) slightly below 300 K is attributed to the dissociative ionization signal of molecular adsorbed CD_3OD in the electron-impact ionizer and to a small impurity of D_2O in CD_3OD, which makes this peak temperature lower than that of the molecularly desorbed CD_3OD TPD peak. With no UV irradiation, a TPD peak at about 520 K is also observed, and it is the result of the recombination desorption of D_2O made from two OD groups on BBO rows that produce water and leave behind an oxygen vacancy (see Figure 3):[28]

$$2DO_{BBO} \xrightarrow{\text{heat}, TiO_2(110)} D_2O(\text{gas}) + \text{BBOv} \tag{4}$$

These D atoms are mainly produced by spontaneous dissociation of CD_3OD at the BBO vacancy (BBOv) sites.[41] As laser irradiation time increases, the D_2O peak from hydroxyl recombination increases in magnitude and the peak gradually shifts to lower temperatures. This shift is related to the increasing D-atom density on BBO sites from the photocatalytic dissociation of CD_3OD adsorbed on the Ti_{5C} sites. It is interesting to point out that oxygen vacancy will be created on the surface after recombination desorption of D_2O from hydroxyl groups on BBO rows.[28,29]

In order to determine if the molecular D_2 product could be formed, TPD spectra at $m/z = 4$ (D_2^+) were measured after 400 nm laser irradiation. Figure 1B shows TPD spectra for four different laser irradiation periods, corresponding to four different $m/z = 4$ (D_2^+) sources. The TPD peak (marked with *) in the spectra slightly below 300 K comes from ionizer fragmentation of CD_3OD (see Figure S2). The D_2^+ signal from this source decreases slightly as the laser irradiation time increases because of the depletion of CD_3OD on the surface. In addition, D_2O could also crack to produce D_2^+ in the ionizer. However, this D_2^+ source is negligible (see Figure S3). The third source of the D_2^+ ion is from the thermally desorbed CD_3 product from dissociatively adsorbed CD_3OD on BBOv sites. This signal appears as a shoulder at ∼630 K in the spectra and should not be dependent on the laser irradiation time.

In addition to the two considerable D_2^+ sources, another obvious source is the thermally desorbed D_2 product formed via recombinative desorption of D atoms on the BBO rows. As indicated in Figure 1B, the TPD peak near 500 K is most likely due to this source. This peak is ∼50 K higher than the recombined D_2O TPD peak and is also strongly dependent on the laser irradiation duration. When the surface temperature is above 450 K, molecularly adsorbed methanol and formaldehyde product on Ti_{5C} have been already desorbed, and only hydrogen atoms on BBO rows and dissociatively adsorbed methanol on BBOv are still present on the surface.[28] Therefore, we can conclude that the 500 K TPD desorption peak at $m/z = 4$ arises from D_2 formation from recombination of D atoms on BBO rows (see Figure 3):

$$2DO_{BBO} \xrightarrow{\text{heat}, TiO_2(110)} D_2(\text{gas}) + 2\text{BBO} \tag{5}$$

We have attempted to detect photodesorbed products at $m/z = 4$ during irradiation, and no signals were detected, suggesting that D_2 product formation is not photodriven. From the above results and previous studies, we thus propose that molecular hydrogen formation from methanol photocatalysis on $TiO_2(110)$ has been the result of three elementary steps: stepwise photocatalytic dissociation of methanol (two steps) and thermal recombination of H atoms on BBO sites. We therefore conclude that hydrogen formation is a process whose rate-determining step is thermally activated recombination, as opposed to an electron- or hole-induced reaction.

In order to evaluate the relative importance of D_2 formation compared to D_2O formation, the yields of D_2O and D_2 as a

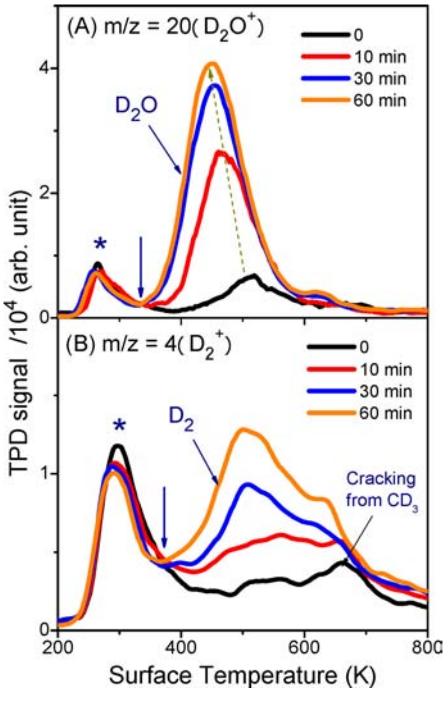

Figure 1. (A) Typical TPD spectra collected at $m/z = 20$ (D_2O^+) following different laser irradiation times at 400 nm. (B) Typical TPD spectra collected at $m/z = 4$(D_2^+) following different laser irradiation times at 400 nm.

function of laser irradiation time have been measured (see Figure 2). The absolute yields of D_2O and D_2 products shown in Figure 2 have been already calibrated based on the detection efficiencies of the two products in the quadrupole mass spectrometer detector. The calibrated result indicates that D_2 formation is clearly less important than D_2O formation. This is consistent with the observation that the desorption of D_2 starts from ~375 K, which is ~50 K higher than that of D_2O. The comparison of TPD temperatures suggests that D_2 formation on $TiO_2(110)$ is more difficult than D_2O formation. This result is fortuitously consistent with previous theoretical calculations, which show that the barrier for H_2 recombinative desorption from BBO sites on $TiO_2(110)$ is ~1.6 eV, which is considerably higher than the barrier (1.10 eV) for H_2O desorption from BBO sites.[42] In ref 42, no H_2 product was detected from the highly hydroxylated $TiO_2(110)$ surface and was attributed to this high energy barrier. From these results, they reached a conclusion that hydrogen recombination is not possible on $TiO_2(110)$, whereas our result clearly indicates that hydrogen recombination on $TiO_2(110)$ can happen. In addition, the observed 50 K difference only in the appearance temperature and the peak temperature between D_2 and D_2O in this work implies that a calculated D_2 recombination barrier of 1.6 eV might be a little too high relative to the D_2O desorption.

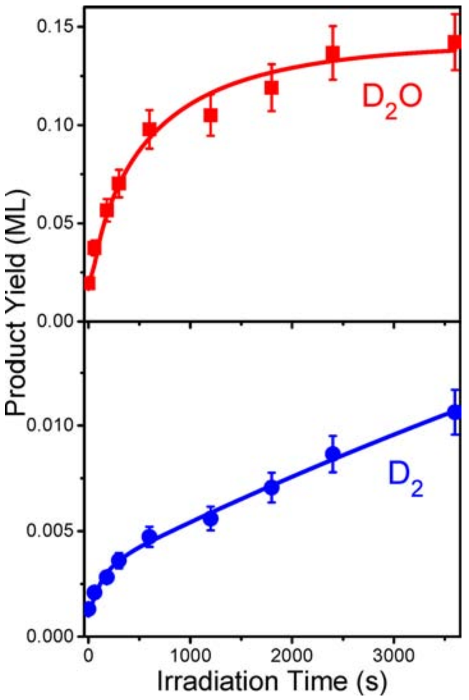

Figure 2. TPD product yield for D_2O and D_2 as a function of irradiation time, derived from data in Figure 1.

In comparison with molecular hydrogen formation from recombination of hydrogen atoms on $TiO_2(110)$ (Figure 3), molecular hydrogen formation on H-atom covered Ru(0001),[43] Ru(001),[44] Pt(111),[45] and Al(111)[46] is much easier and occurs in a temperature range of 250−400 K, which is more than 100 K lower than the temperature for H_2 formation on $TiO_2(110)$. Previous studies[11,33] have demonstrated that noble-metal-modified TiO_2 can indeed enhance the efficiency of hydrogen production with a methanol−water mixture considerably. This implies that hydrogen migrations from TiO_2 to a noble metal surface could facilitate hydrogen production. These earlier results in combination with our new TPD experiments show that molecular hydrogen formation via recombination of H-atoms is probably the rate-determining step in the photocatalytic hydrogen production from methanol on TiO_2.

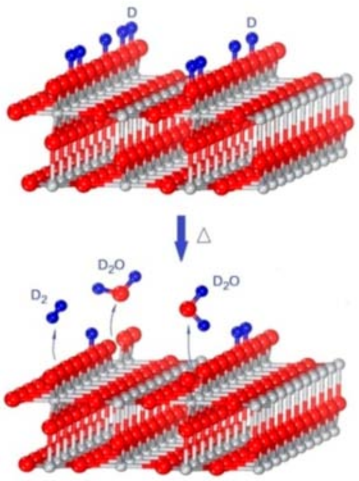

Figure 3. Mechanism of molecular water and molecular hydrogen (deuterium) production from hydrogen atoms on $TiO_2(110)$ surface.

From Figure 2, the rate of D_2O product formation as a function of laser irradiation time is quite different from that of D_2 product. The D_2O yield increases very fast at first and then reaches a plateau, and this yield is anticorrelated well with the depletion of CD_3OD. Since one oxygen defect is created for one D_2O molecule formed during TPD, it appears that BBO defects make D_2O formation more difficult. The D_2 yield, however, increases faster than that of D_2O as the number of BBO defects increases. Hence, more BBO defects created by H_2O recombinative desorption on the surface can make formation of D_2 easier than D_2O formation.

In summary, our experimental investigation provides strong evidence that molecular hydrogen can be produced via a thermal recombination reaction of hydrogen atoms on BBO rows, produced by methanol photocatalysis on rutile $TiO_2(110)$ with 400 nm irradiation, elucidating a possible and universal mechanism for H_2 production with TiO_2-based catalysts. From our experimental results, it clearly shows that water formation from hydroxyl pairs on BBO rows has a lower barrier than molecular hydrogen formation. From the results of this work, we can conclude that lowering the barrier for hydrogen atom recombination is a key point to enhancing hydrogen production and suppressing water formation. Furthermore, adding water to the methanol sample may also help the hydrogen production process by impeding reaction 4 and maintain more H (or D) atoms on the BBO rows.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

TPD data for CD_3OD, CD_2O, and D_2O (Figures S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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