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Article

The role of water in photocatalytic dissociation of methanol on rutile $\text{TiO}_2(110)-(1 \times 1)$

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ABSTRACT

We have performed a surface photocatalysis study of the molecularly adsorbed forms of methanol on a vacuum-annealed rutile $\text{TiO}_2(110)-(1 \times 1)$ surface using temperature-programmed desorption both with and without coadsorbed water to investigate the effect of water and methanol on the photocatalytic dissociation of each other on rutile $\text{TiO}_2(110)-(1 \times 1)$. Our experimental results show conclusively that methanol has no effect on photocatalytic water splitting with water covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface. Further experimental results also show that water does not affect the process of photocatalytic methanol dissociation but does suppress photo-induced desorption of the formaldehyde product of methanol photocatalysis and can enhance the formation of the methyl formate product.

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1. Introduction

Since Fujishima and Honda [1] demonstrated in 1972 that TiO_2 can be used to photocatalytically split water in a photoelectric chemical cell, the application of this material as a catalyst/photocatalyst in water splitting as well as photodegradation of organic molecules has been extensively investigated [2–9]. It is now well known that while pure TiO_2 is photocatalytically inactive for splitting water to produce hydrogen [10], adding methanol can dramatically enhance its photocatalytic activity for hydrogen production [11]. This effect has been attributed to the role of methanol as a hole scavenger or hole trapper allowing efficient separation of the electron-hole pair

to help the separated electrons to catalyze the water splitting reaction.

CH_3OH and H_2O on rutile $\text{TiO}_2(110)-(1 \times 1)$ have served as model systems for surface photocatalytic studies [12–22]. Dohnalek et al. [23] used scanning tunneling microscopy (STM) to show that CH_3OH molecules are molecularly adsorbed on the Ti_{5c} sites and are dissociated only at bridge bonded oxygen (BBO) vacancy sites. These results are consistent with the temperature-programmed desorption (TPD) studies of Henderson and coworkers [13]. Recently, an excited electronic state on the CH_3OH /rutile $\text{TiO}_2(110)-(1 \times 1)$ surface was observed in a two photon photoemission (2PPE) study [24,25], and we attributed this surface state to a photocatalytically dis-

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sociated state of CH_3OH on the surface using combined time-dependent 2PPE (TD-2PPE) and STM [26].

In a very recent study, we have investigated the photocatalysis of CH_3OH and H_2O on rutile $\text{TiO}_2(110)-(1 \times 1)$ using a newly developed universal photocatalysis apparatus in combination with theoretical calculations [27]. Our results indicate that photocatalytic dissociation of CH_3OH of rutile $\text{TiO}_2(110)-(1 \times 1)$ occurs on the Ti_{5c} sites in a stepwise manner, in which the O–H dissociation proceeds first and is then followed by C–H dissociation. As a result, product formaldehyde (CH_2O) is formed in the photocatalysis of CH_3OH . This picture can be readily explained by theoretically calculated ground state reaction pathways. However, under exactly the same experimental conditions, photocatalytic dissociation of H_2O on rutile $\text{TiO}_2(110)-(1 \times 1)$ has not been detected. Shen and Henderson [21] recently attempted to investigate this issue and detected no photocatalytic dissociation of either CH_3OH or H_2O [23]. This is likely due to the weak light source used in their photocatalysis experiment. To understand whether CH_3OH could aid H_2O splitting or H_2O could affect CH_3OH dissociation, we have carried out a cautious experimental study on a mixed $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface using the same photocatalysis apparatus as that reported in Ref. [27].

2. Experimental

The TPD apparatus has been previously described [27]. The base pressure of the sample chamber was $< 6 \times 10^{-11}$ Torr. A quadrupole mass spectrometer (Extrel) was 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 experiments. The rutile $\text{TiO}_2(110)-(1 \times 1)$ (Princeton Scientific) single crystal had dimensions of $10 \text{ mm} \times 10 \text{ mm} \times 1 \text{ mm}$. The surface was cleaned by cycles of Ar^+ sputtering and resistive heating to 850 K in vacuum until any contamination was below the detection limit of AES and a well-ordered rutile $\text{TiO}_2(110)-(1 \times 1)$ LEED pattern with a low background was observed. The rutile $\text{TiO}_2(110)-(1 \times 1)$ surface contained 3%–4% O-vacancy defects as determined by H_2O TPD. 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 $\sim 100 \text{ K}$ during CH_3OH dosing and subsequent UV irradiation.

The irradiating light came from a frequency doubled Ti:Sapphire femtosecond laser at 400 nm (coherent, repetition rate 1 kHz). The average intensity on the sample was about $7.2 \times 10^{17} \text{ photons cm}^{-2} \text{ s}^{-1}$ (200 mW). The 400 nm laser used for surface irradiation in this experiment had a beam diameter of 6 mm and an incident angle of $\sim 30^\circ$ with respect to the rutile $\text{TiO}_2(110)-(1 \times 1)$ surface, which was mounted with an angle point at the top. Using 200 mW laser power, the TiO_2 surface temperature was increased to $\sim 150 \text{ K}$ from the base surface temperature of $\sim 100 \text{ K}$. TPD measurements of the various surface products were then made to probe the photocatalytic products that stayed on the surface after photoirradiation, while time-of-flight measurements were used to probe gaseous

species produced from the surface during laser irradiation.

3. Results and discussion

Figure 1 (a) shows the selected TPD spectra at a mass-to-charge ratio (m/z) of 31 (CH_2OH^+) after the clean rutile $\text{TiO}_2(110)-(1 \times 1)$ surface was dosed with 0.3 ML ($1 \text{ ML} = 5.2 \times 10^{14} \text{ molecules cm}^{-2}$) of CH_3OH and 0.2 ML of H_2O , and was then irradiated by the 400 nm laser for different periods of time. The main peak around 310 K in the spectra is due to molecular CH_3OH desorption from Ti_{5c} sites. From the TPD spectra it is obvious that 400 nm laser irradiation depleted the CH_3OH TPD signal. The integrated TPD signals for this peak at different irradiation times are shown in Fig. 1 (b) and clearly indicate that the TPD signal decreased monotonically as laser irradiation time increased. This implies that the CH_3OH molecules adsorbed on the Ti_{5c} sites were photocatalytically dissociated. After 60 min laser irradiation, about 20% of the CH_3OH molecules on the surface were dissociated.

We also made similar measurements for 0.3 ML CH_3OH only covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface for comparison. The CH_3OH TPD peak depletion as a function of laser irradiation

Fig. 1. (a) TPD spectra taken at $m/z = 31$ at four different laser irradiation times; (b) Integrated signal of the TPD peak at 315 K at mass 31 after the $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface was irradiated with 400 nm laser light for different periods of time.

Fig. 2. (a) TPD spectra taken at $m/z = 31$ (CH_2OH^+) at four different laser irradiation times for the 0.3 ML CH_3OH covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface; (b) The integrated signal of the TPD peak at 315 K at mass 31 shown in (a) after the surface was irradiated with 400 nm laser light for different periods of time.

time (Fig. 2) on this surface was very similar to that for the 0.3 ML $\text{CH}_3\text{OH} + 0.2$ ML H_2O covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface. Furthermore, we also measured the CH_3OH TPD peak depletion as a function of laser irradiation time for the 0.3 ML $\text{CH}_3\text{OH} + 0.4$ ML H_2O covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface (Fig. 3). In fact, the results of CH_3OH TPD peak depletion on these three surface samples are all similar (Fig. 4). This indicates that the presence of H_2O on the rutile $\text{TiO}_2(110)-(1 \times 1)$ surface does not affect CH_3OH photocatalytic dissociation process in a significant way.

In addition, we also observed the CH_2O product (270 K TPD peak) from the photocatalysis of CH_3OH (Fig. 5 (a)) for the same surface, which is clearly produced via the stepwise photocatalytic dissociation of CH_3OH on rutile $\text{TiO}_2(110)-(1 \times 1)$ [27]:

The above results indicate that CH_3OH photocatalysis in the presence of H_2O is very similar to that of CH_3OH photocatalytic dissociation on the same surface without H_2O . It is interesting to point out that methoxy (CH_3O) is a key intermediate in

Fig. 3. (a) TPD spectra taken at $m/z = 31$ at four different laser irradiation times for the 0.3 ML $\text{CH}_3\text{OH} + 0.4$ ML H_2O covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface; (b) The integrated signal of the TPD peak at 315 K at mass 31 shown in (a) after the surface was irradiated with 400 nm laser light for different periods of time.

Fig. 4. The integrated signal of the TPD peak at 315 K at $m/z = 31$ shown in Figs. 1, 2, and 3 after the three different surfaces (0.3 ML CH_3OH /rutile $\text{TiO}_2(110)-(1 \times 1)$, 0.3 ML $\text{CH}_3\text{OH} + 0.2$ ML H_2O /rutile $\text{TiO}_2(110)-(1 \times 1)$, 0.3 ML $\text{CH}_3\text{OH} + 0.4$ ML H_2O /rutile $\text{TiO}_2(110)-(1 \times 1)$) were irradiated with 400 nm laser light for different periods of time. The integrated signals shown were all normalized at time zero.

CH_3OH photocatalytic dissociation. The presence of CH_3O is also indirectly confirmed by photocatalytic synthesis of methyl

Fig. 5. (a) TPD spectra taken at $m/z = 30$ at four different laser irradiation times for 0.3 ML $\text{CH}_3\text{OH} + 0.2$ ML H_2O covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface; (b) TPD spectra taken at $m/z = 30$ at four different laser irradiation times for 0.3 ML CH_3OH only covered $\text{TiO}_2(110)$ surface.

formate (HCOOCH_3) via cross coupling of CH_2O and CH_3O on rutile $\text{TiO}_2(110)-(1 \times 1)$ [28,29].

For the CH_2O product formation process, we compared the CH_3OH covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface with the 0.3 ML $\text{CH}_3\text{OH} + 0.2$ ML H_2O covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface. Figure 5(b) shows several TPD spectra at $m/z = 30$ (H_2CO^+) for 0.3 ML of CH_3OH covered surface in comparison with that obtained for a 0.3 ML $\text{CH}_3\text{OH} + 0.2$ ML H_2O coadsorbed surface. The results are very intriguing. It appears that the signal level of CH_2O TPD product for CH_3OH and H_2O coadsorbed surface is noticeably smaller (about 1.5 times smaller) than that for the surface only covered with CH_3OH . To trace the origin of this phenomenon, we also carried out time of flight (TOF) measurements for photodesorbed products at $m/z = 30$ (Fig. 6) and found that photo-induced desorption of the CH_2O product by 400 nm light was also noticeably smaller for the CH_3OH only adsorbed surface. The integrated TOF signal between 0 to 150 s is incidentally about 1.5 times smaller for the CH_3OH only adsorbed surface. These results seem to indicate that photo-induced desorption of CH_2O products was suppressed by the presence of water. This implies that water acted as an efficient energy absorber so that less energy was available for formaldehyde product photo-desorption. These results also suggest that water actually affects the gaseous formaldehyde formation process in methanol photocatalysis on rutile $\text{TiO}_2(110)-(1 \times 1)$

Fig. 6. Time of flight (TOF) data for photodesorbed products at $m/z = 30$ (CH_2O^+) during laser irradiation for 0.3 ML CH_3OH covered $\text{TiO}_2(110)$ surface and the 0.3 ML $\text{CH}_3\text{OH} + 0.2$ ML H_2O covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface.

Fig. 7. (a) TPD spectra taken at $m/z = 18$ at four different laser irradiation times; (b) Integrated signal of the TPD peak at 260 K at $m/z = 18$ after the $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface was irradiated with 400 nm laser light for different periods of time.

even though it does not seem to affect the photocatalytic dissociation step.

To determine whether CH_3OH or CH_3O have any enhancing effect on water splitting on rutile $\text{TiO}_2(110)-(1 \times 1)$, we also measured the TPD signal at mass 18 (H_2O^+) for the rutile $\text{TiO}_2(110)-(1 \times 1)$ surface covered with 0.3 ML of CH_3OH and 0.2 ML of H_2O at different laser irradiation times. Figure 7(a)

shows a few typical TPD spectra at mass 18 (H_2O^+) with laser irradiation times of 0 to 60 min. The main feature around 260 K in the spectra is due to the desorption of molecular H_2O from $\text{Ti}_{5\text{c}}$ sites. From the TPD spectra, it is clear that 400 nm laser irradiation shifts this feature slightly towards lower temperature. This shift is caused by the increasing density of H atoms on the BBO sites because of CH_3OH dissociation. The peak height of the main feature, however, did not change much with laser irradiation time. We integrated this main peak in the TPD at different irradiation times, as shown in Fig. 7(b). In the presence of CH_3OH , the main H_2O TPD peak intensity at $m/z = 18$ did not change within the experimental uncertainty. We also measured the H_2O TPD spectra and total TPD signal of the main peak at 260 K as a function of laser irradiation time for the 0.3 ML CH_3OH + 0.4 ML H_2O covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface (Fig. 8). The obtained result is nearly identical to that of the 0.3 ML CH_3OH + 0.2 ML H_2O covered surface. These experimental results clearly show that CH_3OH cannot enhance water splitting at 400 nm on rutile $\text{TiO}_2(110)-(1 \times 1)$ in a noticeable way. In addition, because CH_3O is also present as a key intermediate in the photocatalytic dissociation of CH_3OH , our results imply that CH_3O has no effect in enhancing photocatalytic H_2O dissociation on TiO_2 .

Previous studies demonstrate that photocatalytic synthesis

Fig. 8. (a) TPD spectra taken at $m/z = 18$ at four different laser irradiation times for the 0.3 ML CH_3OH + 0.4 ML H_2O covered rutile $\text{TiO}_2(110)-(1 \times 1)$ surface; (b) Integrated signal of the TPD peak at 260 K at $m/z = 18$ shown in the upper panel after the surface was irradiated with 400 nm laser light for different periods of time.

of HCOOCH_3 via cross coupling of CH_2O and CH_3O happens on 0.5 ML of CH_3OH covered $\text{TiO}_2(110)$ [28,29]. In this work, no HCOOCH_3 was formed with only 0.3 ML of CH_3OH covered rutile $\text{TiO}_2(110)-(1 \times 1)$ due to low CH_3OH coverage. However, with increasing coverage of coadsorbed H_2O , a little shoulder became obvious at the low temperature edge of the 315 K peak in the mass 31 TPD trace. Although the shoulder is very small, its presence implies that H_2O can enhance the efficiency of photocatalytic synthesis of HCOOCH_3 by occupying $\text{Ti}_{5\text{c}}$ sites on the surface and thereby increase the opportunity that CH_2O and CH_3O are adjacent to each other, similar to recent observations on noble metal modified TiO_2 photocatalysts [30].

For TiO_2 , separated holes and electrons generated by photons are believed to be the driving force for reaction, desorption, and so on [7]. Our results show that the desorption temperature of H_2O and product CH_2O are 260 and 270 K for CH_3OH and H_2O coadsorbed rutile $\text{TiO}_2(110)-(1 \times 1)$, respectively. TOF measurements only observe photo-induced desorption of the CH_2O product, which can be inhibited by the presence of H_2O . These phenomena indicate that photo-induced desorption of the CH_2O product is not only a simple hole or electron driven process. Previous studies [31,32] demonstrate that H_2O molecules can form hydrogen bonds with bridging oxygen sites or H_2O molecules on rutile $\text{TiO}_2(110)-(1 \times 1)$. Here, no observation of TOF signal of H_2O suggests that the excitation energy for H_2O desorption may be relaxed by complicated hydrogen bonds or hydrogen bond network, as well as decreased TOF signal of CH_2O when H_2O is present on rutile $\text{TiO}_2(110)-(1 \times 1)$. Thus, a few issues need to be closely examined. Primarily, there is clearly a need to clarify the exact picture of how separated holes and electrons, or even phonons created by hole and electron recombination, interact with reactants and the energy transfer channel for reaction, desorption, and so on.

4. Conclusions

Photocatalytic dissociation of CH_3OH on rutile $\text{TiO}_2(110)-(1 \times 1)$ occurs through O–H bond and C–H bond cleavage in adsorbed CH_3OH , yielding CH_2O and two surface OH groups. Coadsorbed H_2O does not promote photochemistry for molecularly adsorbed CH_3OH , and coadsorbed CH_3OH does not affect H_2O photoactivity. However, coadsorbed H_2O can enhance formation of the HCOOCH_3 product. H_2O molecules hydrogen-bonded to bridging oxygen sites or CH_2O may be the cause of the inhibited photo-induced desorption of CH_2O , suggesting that hydrogen bonds may play an important role in energy transfer. Further work is needed to focus on the role of hydrogen bonds.

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Graphical Abstract

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The role of water in photocatalytic dissociation of methanol on rutile $\text{TiO}_2(110)-(1 \times 1)$

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Coadsorbed water on methanol covered $\text{TiO}_2(110)-(1 \times 1)$ surface has nearly no effect on methanol photodissociation.

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水对甲醇在Rutile- $\text{TiO}_2(110)-(1 \times 1)$ 表面光催化解离的影响

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摘要: 采用程序升温脱附方法研究了甲醇分子吸附在真空退火后的二氧化钛(110)表面的光催化过程, 对比分析了单独吸附甲醇

分子以及甲醇分子与水分子共吸附情况下的光催化解离过程. 结果表明, 在二氧化钛(110)表面吸附的甲醇分子对共吸附水分子的光催化解离过程并没有直接的帮助作用. 共吸附状态下的水分子也同样没有影响到甲醇的光致解离过程, 但是水分子的存在抑制了甲醇光解产物甲醛的光致脱附过程, 同时促进了甲酸甲酯的形成.

关键词: 甲醇; 水; 金红石二氧化钛(110)-(1 × 1)表面; 光催化; 程序升温脱附; 甲醛

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