Photocatalytic Dissociation of CH$_3$OH on ZnO(0001) Surface

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Photocatalysis of CH$_3$OH on the ZnO(0001) surface has been investigated by using temperature-programmed desorption (TPD) method with a 266 nm laser light. TPD results show that part of the CH$_3$OH adsorbed on ZnO(0001) surface are in molecular form, while others are dissociated. The thermal reaction products of H$_2$, CH$_3$, H$_2$O, CO, CH$_2$O, CO$_2$ and CH$_3$OH have been detected. Experiments with the UV laser light indicate that the irradiation can promote the dissociation of CH$_3$OH/CH$_3$O to form CH$_2$O, which can be further converted to HCOO$^-$ during heating or illumination. The reaction between CH$_3$OH$_{Zn}$ and OH$_{ad}$ can form the H$_2$O molecule at the Zn site. Both temperature and illumination promote the desorption of CH$_3$ from CH$_3$O. The research provides a new insight into the photocatalytic reaction mechanism of CH$_3$OH on ZnO(0001).

Key words: Methanol, Photocatalysis, ZnO(0001) surface, Temperature-programmed desorption

I. INTRODUCTION

Methanol (CH$_3$OH) is a common material in our daily life and industrial production [1]. As the simplest saturated monohydric alcohol, it is often selected as a probe molecule to study the surface active sites and catalytic reactivities of various metal oxide catalysts [2]. Meanwhile, it can be converted into H$_2$ in heterogeneous photocatalysis process, which is a potential way to provide clean energy resource [3–6]. Zinc oxide (ZnO), as an n-type semiconductor material with wide bandgap of ~3.37 eV [7, 8], has attracted enormous interest in the past decades due to its potential applications, such as heterogeneous photocatalysis, gas sensors, and optoelectronic devices [9–12]. Thus, to study the adsorption and reaction of CH$_3$OH on ZnO is not only helpful to explore the catalytic properties of ZnO, but also important for understanding the fundamental processes of ZnO photocatalysis.

In the hexagonal wurtzite ZnO crystal structure, there are two types of low-index surfaces, namely, the non-polar and polar surfaces. ZnO(1010) is one of the non-polar surfaces, which is electrostatically stable and is obtained by dividing the same number of Zn and O bond [13, 14]. It has been well established that part of CH$_3$OH dissociatively adsorbs on different ZnO single crystal surfaces to produce methoxy (CH$_3$O) [15]. Corresponding theoretical studies about CH$_3$OH adsorption on ZnO(0001) suggest that the adsorption energy of molecular CH$_3$OH on this surface is only about 0.6 eV, whereas, the adsorption energy of CH$_3$O groups is as high as 3.12 eV when the oxygen atom binds to a Zn atom, demonstrating that the dissociative adsorption state of CH$_3$OH on ZnO(0001) is much more stable than the molecular adsorption state [16, 17]. Jin and coworkers reported that only a small number of CH$_3$OH dissociatively adsorb on the defect sites of ZnO(1010) surface, producing CH$_3$O groups, which further decompose into formaldehyde (CH$_2$O), CO, and H$_2$ at high temperature [18]. On the other hand, the two polar crystal planes (ZnO(0001) and ZnO(0001)) possess a non-zero dipole moment along the [0001] direction and are therefore considered to be very intriguing [19]. Vohs and Barteau have shown that ZnO(0001) has no catalytic activity for the decomposition of CH$_3$OH by using the temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) [20]. Nevertheless, in subsequent experiments studies, it was found that the defective ZnO(0001) surface is catalytically active for the decomposition of CH$_3$OH into H$_2$, CO, CH$_2$O, and H$_2$O [18]. Scanning tunneling microscopy (STM) images of the clean ZnO(0001) surface provide direct evidence that surface reconstruction changes the sto-
chiometric ratio to produce Zn vacancies on the surface and effectively remove the electrostatic instability \cite{13, 14, 21, 22}. In addition, the results obtained from TPD, XPS, and high resolution electron energy loss spectroscopy (HREELS) suggest that the ZnO(0001) surface can oxidize CH$_3$OH to H$_2$, HCOO$^-$, CO and CH$_2$O from CH$_3$O groups and to CO or CO$_2$ by formate intermediate (HCOO$^-$) \cite{18, 20}. These studies have demonstrated that ZnO(0001) surface has an excellent catalytic effect on the oxidation of CH$_3$OH.

As an environmental friendly photocatalyst, ZnO has shown great potential to degrade organic compounds and its photocatalytic activity is anticipated to be similar to TiO$_2$ \cite{23, 24}. It is generally believed that the structure and morphological characteristics affect the photocatalytic properties of semiconductor \cite{25, 26}. Likewise, DFT calculations indicate that the photocatalytic activity of ZnO(0001) surface is higher than other low-index surfaces \cite{27}. Wu and coworkers found that ordered crystal surfaces of ZnO is photoactive for the degradation of methylene blue, but the ability of photocatalytic degradation of organic compounds disappears when the ordered surfaces are dissolved \cite{28}.

Although the thermochemical reaction of CH$_3$OH on the ZnO(0001) surface has been deeply studied, the photochemical reaction has not been extensively studied on this surface and its mechanism remains unclear yet. Therefore, it is of great significance to investigate the photocatalytic reaction of CH$_3$OH on the ZnO(0001) surface at a molecular level for better understanding ZnO photocatalysis. In this work, we have investigated the photochemistry of CH$_3$OH on ZnO(0001) surface by using a 266 nm femtosecond laser at low temperature. The results of the research have proven that Zn-terminated ZnO(0001) surface is highly active for the dissociation of CH$_3$OH and CH$_2$O.

II. EXPERIMENTS

The experiment was carried out in an ultrahigh vacuum (UHV) chamber with base pressure better than 6×10$^{-10}$ Torr. The ZnO(0001) crystal (obtained from HF-Kejing, 10 mm×10 mm×1 mm) was fixed to a Ta metal plate. A NiCr-Ni thermocouple was glued directly to the ZnO(0001) surface by Ceramic adhesive (Ceramabond 503, Aremco Products). The sample surface was cleaned by cycles of Ar$^+$ sputtering followed by UHV annealing for 20 min. A well-ordered (1×1) LEED pattern was observed, similar to previous LEED result of the ZnO(0001) surface \cite{13}. The purity of CH$_3$OH was 99.9\% (Sigma-Aldrich). Before being introduced into the main chamber with a calibrated molecular beam doser, it was further purified by several freeze-pump-thaw cycles. All the TPD studies were conducted with a heating rate of 2 K/s. The 266 nm light came from a frequency tripling Ti: Sapphire femtosecond laser (Coherent, repetition rate: 1 kHz). The laser had a pulse width of ~100 fs. The average power of the laser light was 60 mW, corresponding to \~1.4×10$^{17}$ photons-cm$^{-2}$ ·s$^{-1}$.

FIG. 1 TPD spectra collected at m/z=32 (CH$_3$OH$^+$) after the clean ZnO(0001) surface was dosed with various amount of CH$_3$OH at 120 K (1 ML=1.09×10$^{15}$ molecule/cm$^2$).

III. RESULTS AND DISCUSSION

A. The adsorption and reaction of CH$_3$OH on ZnO(0001) surface

FIG. 1 shows the TPD spectra collected at a mass-to-charge ratio of 32 (CH$_3$OH$^+$) after the clean ZnO(0001) surface was dosed with different amount of CH$_3$OH at 120 K. At the highest coverage, four desorption features at 138, 190, 245, and 330 K are observed. Based on the work of CH$_3$OH adsorption on the ZnO(0001) surface done by Jin and coworkers using thermal desorption spectroscopy (TDS) and HREELS method \cite{15}, the four obvious desorption features can be assigned to multilayer desorption, bilayer desorption, submonolayer desorption, and recombinative desorption of CH$_3$OH groups.

Other products from CH$_3$OH decomposition on the ZnO(0001) surface are also detected during the TPD process. As shown in FIG. 2, a series of TPD traces were collected at m/z=2 (H$_2^+$), 15 (CH$_4^+$), 18 (H$_2$O$^+$), 28 (CO$^+$), 30 (CH$_2$O$^+$), 31 (CH$_3$O$^+$), 32 (CH$_3$OH$^+$), and 44 (CO$_2^+$) after 0.53 ML CH$_3$OH adsorbed on the ZnO(0001) surface at 120 K. The TPD peak at 330 K (m/z=15, 31, 32) is due to the desorption of CH$_3$OH. No TPD signals are observed at m/z=46 and 60, suggesting that no HCOOH and HCOOCH$_3$ are formed during the TPD process. Conversely, thermal products of H$_2$, H$_2$O, CO, CH$_2$O, and CO$_2$ are detected in the TPD traces of m/z=2, 18, 28, 30, and 44, respectively. According to previous work of CH$_3$OH desorption on ZnO(0001) and ZnO(0001), the ZnO(0001) surface is lack of reactivity due to the absence of accessible acid-
base site pairs being necessary for dissociative adsorption on this surface [20]. However, the reconstructed ZnO(0001)-(1×3) surface exhibits high catalytic activity for CH₃OH dissociation and decomposition, which produces H₂, CO, CH₂O at 590 and 660 K, CO₂ at 590 K, and H₂O at 610 and 690 K via the following ways [18]:

\[
\text{CH}_3\text{OH}_{\text{Zn}} + \text{O}_{\text{surface}} \rightarrow \text{CH}_3\text{OZn} + \text{OH}_{\text{ad}}
\]

CO₂ at 590 K:

\[
\text{CH}_3\text{OZn} + \text{O}_{\text{surface}} \rightarrow \text{HCOOZn} + \text{H}_2\text{ad}
\]

H₂O at 610 and 690 K:

\[
\text{OH}_{\text{ad}} + \text{OH}_{\text{ad}} \rightarrow \text{H}_2\text{O}_g + \text{O}_{\text{surface}}
\]

However, on the ZnO(0001)-(1×1) surface, CH₃OH dissociation and decomposition produce H₂ and CH₂O at 520 K, CO at 520 and 565 K, CO₂ at 565 K, and H₂O at 575 K via the following ways [18]:

H₂, CO, CH₂O at 590 and 660 K:

\[
\text{CH}_3\text{OZn} + \text{O}_{\text{surface}} \rightarrow \text{CH}_2\text{OZn} + \text{OH}_{\text{ad}}
\]

\[
\text{CH}_3\text{OZn} \rightarrow \text{CH}_2\text{O}_g
\]

\[
\text{CH}_2\text{OZn} \rightarrow \text{CO}_g + \text{H}_2\text{g}
\]

H₂O at 575 K:

\[
\text{OH}_{\text{ad}} + \text{OH}_{\text{ad}} \rightarrow \text{H}_2\text{O}_g + \text{O}_{\text{surface}}
\]

The desorption temperatures of H₂, CO, CH₂O, CO₂, and H₂O products are nearly the same as the results obtained on ZnO(0001) surface [18, 30–32]. In addition, a new desorption peak of H₂O is observed at 350 K with a yield of 0.042 ML, which is much higher than the amount of the impurity in CH₃OH sample (<0.1%), indicating that the 350 K peak may be due to surface reaction. The source of this peak will be discussed below in detail. The results clearly demonstrate that the CH₃OH decomposition occurs on the ZnO(0001) surface in our experiment.

B. Photocatalytic chemistry of CH₃OH on ZnO(0001) surface

As mentioned above, both experimental and theoretical results demonstrate that part of CH₃OH molecules dissociatively adsorb on the ZnO(0001) surface to produce CH₃O groups and H atoms. Based on previous study of CH₃OH adsorption and photodissociation on TiO₂ single crystal surfaces, CH₃O groups have higher photo reactivity than CH₃OH molecules [4, 33]. Thus, high photo reactivity of CH₃O groups on ZnO(0001) is also expected.

FIG. 3 shows typical TPD spectra collected at m/z=32 (CH₃OH⁺), 30 (CH₃O⁺) and 2 (H₂⁺) as a function of irradiation time after adsorbing 0.53 ML CH₃OH on the ZnO(0001) surface. With increasing irradiation time, the 330 K peak in FIG. 3(a) decreases rapidly, suggesting that CH₃OH molecules are photodissociated or phothesized during the irradiation. Correspondingly, the high temperature peaks of CH₂O and H₂ at 510 K produced via CH₃O group decomposition also decrease fast, indicating that CH₃O groups on the surface are also depleted. Consequently, the decrease of the CH₃OH and CH₂O groups on the surface, a new desorption peak at about 310 K appears and increases first and then decreases as the illumination time increases, which is attributed to CH₂O formation.

\[
\text{CH}_3\text{OH}_{\text{Zn}} + \text{O}_{\text{surface}} + \text{hv} \rightarrow \text{CH}_2\text{OZn} + \text{CH}_2\text{O}_g + \text{OH}_{\text{ad}}
\]

Nevertheless, the decrease of the 510 K peak in the TPD traces of m/z=30 is much faster than the 330 K peak in the TPD traces of m/z=32, clearly demonstrating that the photo reactivity of CH₃O groups on the surface is...
much higher than that of CH$_3$OH molecules, in agreement with the results on the TiO$_2$ surfaces [4, 33]. The photolysis of CH$_3$OH into CH$_3$O occurs in a stepwise mechanism, in which the O–H bond cleavage of CH$_3$OH molecules occurs via a thermochemical process first and then the C–H bond cleavage of CH$_3$OH molecules occurs via a photochemical process.

However, the yield of CH$_3$O production (310 K peak) upon irradiation is much less than the depletion of CH$_3$OH and CH$_3$O groups, indicating that part of CH$_3$OH and CH$_3$O product are photodesorbed during irradiation. Consequently, photo stimulated desorption signals of various species were monitored by time of flight (TOF) method during the irradiation process, as shown in FIG. 4. The TOF signal of m/z=32 can be only from CH$_3$OH desorption. The TOF signals of m/z=15 and 30 are about 4 and 5 times bigger than that of m/z=32, respectively. Actually, the respective relative intensity of the ion fragments at m/z=15, 30 and 32 for CH$_3$OH molecules is about 0.375:0.118:1 in our mass spectrometer. Hence, most of the TOF signal at m/z=30 comes from photo induced CH$_3$O product desorption, which is initiated from CH$_3$OH/Zn/CH$_3$O$_2$ dissociation. Whereas, the big TOF signal at m/z=15 (CH$_3^+$) suggests that the C–O bond scission of CH$_3$OH/CH$_3$O$_2$ may perhaps occur by ejecting CH$_3$ into vacuum and leaving behind O$_{Zn}$/OH$_{Zn}$ on the surface during the 266 nm illumination.

CH$_3$OH$_{Zn}$/CH$_3$O$_2$ + h$_\nu$ → O$_{Zn}$/OH$_{Zn}$ + CH$_3^+$ (18)

Based on previous work about H atom desorption on ZnO(0001), the recombinative desorption of H$_2$ occurs at about 450 K [34]. Although CH$_3$OH/CH$_3$O$^+$ photolysis can produce CH$_2$O and OH$_{ad}$, no desorption signal of H$_2$ is observed at about 450 K after irradiation. This indicates that the dissociated H atoms may be desorbed in the form of other species. Accordingly, other possible TPD traces at different masses were collected. As shown in FIG. 5(a), two desorption peaks at 350 and 575 K are observed in the TPD trace of H$_2$O on 0.53 ML CH$_3$OH covered ZnO(0001) surface before irradiation. The high temperature one is due to recombinative desorption of OH$_{ad}$, and the low temperature one is due to the desorption of H$_2$O on the Zn sites of the surface [15]. Upon irradiation, the intensities of both the two peaks increase with irradiation time. While, O$_{Zn}$/OH$_{Zn}$ species may be produced by reaction (18), thus, the 350 K peak may be due to the reaction of OH$_{ad}$ and O$_{Zn}$/OH$_{Zn}$:

OH$_{ad}$ + O$_{Zn}$/OH$_{Zn}$ → H$_2$O$_{Zn}$ + O$_{surface}$ (19)

Obviously, no O$_{Zn}$/OH$_{Zn}$ will be produced without irradiation. According to previous work about CH$_3$OH adsorption on anatase TiO$_2$(101), the reaction between CH$_3$OH molecules on the regular Ti sites and H atoms on the lattice O atoms can produce H$_2$O molecules on the regular Ti sites and CH$_3$ on the lattice O atoms [4]. In this work, the production of H$_2$O$_{Zn}$ at 350 K may also occur via the similar reaction:

CH$_3$OH$_{Zn}$/H$_2$O$_{ad}$ + /O$_{ad}$ → H$_2$O$_{Zn}$ + CH$_3$O$_{surface}$ (20)

Then, the CH$_3$O$_{surface}$ will be desorbed in the form of CH$_3^+$ at high temperature. Correspondingly, a broad desorption peak of CH$_3^+$ in the temperature range of 450–750 K is observed (FIG. 5(b)). Moreover, the intensity of the peak initially increases with irradiation...
FIG. 5 The ZnO(0001) surface was dosed with 0.53 ML CH$_3$OH at 120 K. TPD spectra collected at (a) $m/z=18$ (H$_2$O$^+$) and (b) $m/z=15$ (CH$_3^+$) after different irradiation time with 266 nm laser.

FIG. 6 The ZnO(0001) surface was dosed with 0.53 ML CH$_3$OH at 120 K. (a) TPD spectra collected at (a) $m/z=28$ (CO$^+$) and (b) $m/z=44$ (CO$_2^+$) after different irradiation time with 266 nm laser.

time and then starts to decrease at longer irradiation time. The increase of this peak indicates that the reaction (20) may occur, and the decrease is due to the desorption of CH$_3$ on the O$_{\text{surface}}$ sites during irradiation. Thence, reaction (18) could be rewritten as:

$$\text{CH}_3\text{O}_{\text{surface}} + h\nu \rightarrow \text{CH}_3^+ + \text{O}_{\text{surface}} \quad (21)$$

However, the possibility of reactions (18, 19) can not be totally ruled out.

In addition, photodesorption products at $m/z=28$ and 44 are also detected. The product at $m/z=44$ can be only from CO$_2$ desorption. Undoubtedly, the product at $m/z=28$ may come from three sources. The first two are the ion fragments of CH$_3$OH and CH$_2$O in the mass spectrometer, respectively. The last one is from CO desorption. The intensity of the TOF signal at $m/z=28$ is much bigger than that at $m/z=30$ and 32 (FIG. 4), demonstrating that part of the TOF signal at $m/z=28$ is due to photo induced CO desorption. The appearance of CO and CO$_2$ products indicates that HCOO product may perhaps further react to produce CO and CO$_2$. Besides, the TPD spectra of CO and CO$_2$ were collected on the CH$_3$OH covered ZnO(0001) surface after irradiating the surface for different time (FIG. 6).

Before irradiation, the low temperature desorption peaks of CO at 150 K and CO$_2$ at 360 K are due to the adsorption of CO and CO$_2$ in the background. After 0.5 min irradiation, the CO peak at 150 K decreases significantly, which is attributed to photoinduced CO desorption. While, the 555 K peak increases a little, revealing that the amount of HCOO$^-$ on the surface increases, which may be attributed to photoinduced CH$_3$O groups decomposition. After 5 min irradiation, the 555 K peak is nearly saturated. Additionally, the desorption of CO is still observed for longer irradiation time, suggesting that HCOO$^-$ or CH$_3$O products may further photo-decompose into CO. In the case of CO$_2$ at 360 K, there are two sources. One is from the adsorption of CO$_2$ from the background during irradiation. The other is from photoinduced HCOO$^-$ decomposition. What’s more, the high temperature CO$_2$ peak at 560 K increases a little with irradiation time, similar to the trend of the increase of CO desorption peak at 555 K. Additionally, the intensity of the 560 K peak is much smaller than that of the 555 K, illustrating that HCOO$^-$ mainly decomposes into CO during the TPD process. Although CH$_3$OH photolysis on ZnO(0001) is much more complicated than that occurs on rutile TiO$_2$(110) and anatase TiO$_2$(101) [4, 29, 35], the results clearly show that ZnO(0001) has highly photocatalytic activity for CH$_3$OH dissociation and CH$_2$O decomposition. However, the big bandgap is the main disadvantage for ZnO as a good photocatalyst. Besides, Kung and co-workers found that the structure sensitivity in CH$_3$OH decomposition on ZnO single crystal surfaces [36, 37]. The ZnO(0001) surface used in our experiment is highly reconstructed with many high-density triangularly shaped pits and islands of different sizes on it. All the step edges on the polar ZnO(0001) surface are one-layer-high and O-terminated [13, 21]. Only those CH$_3$OH molecules adsorbing on the Zn atoms at the step edges have opportunity to dissociate into CH$_3$O groups and H atoms. In other words, only the O atoms at step edges are under coordinated, which have the capacity to accommodate dissociated H atoms. Ergo, the Zn atoms at the step edges are the active sites for CH$_3$OH thermochemistry and photochemistry reaction on ZnO(0001). Besides, the size of the islands is strongly dependent on the process of sample preparation [33]. For example, annealing at higher temperature
(\(\sim 750\ ^\circ\mathrm{C}\)) will make the terraces wider and the triangular pits smaller, then the pit density and the number of triangle islands increase \([13]\), which will make the surface being highly reduced and further affect the ratio of reaction channels effectively. In the process of HCOO\(^-\) decomposition, the selectivity of CO or CO\(_2\) depends on the degree of local surface reduction, and the reductive surface is favorable to the formation of CO \([20]\).

IV. CONCLUSION

In this study, we have investigated CH\(_3\)OH photolysis on the ZnO(0001) surface under 266 nm UV irradiation. The CH\(_3\)OH photolysis occurs easily on this surface, forming CH\(_2\)O via a stepwise mechanism. CH\(_3\)O groups show much higher photo reactivity than CH\(_3\)OH molecules. While, CH\(_2\)O could further decompose into HCOO\(^-\), CO and CO\(_2\), demonstrating the prospect of ZnO as a photocatalyst for the degradation of organic molecules.

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