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Diffusion of Formaldehyde on Rutile $\text{TiO}_2(110)$ Assisted by Surface Hydroxyl Groups

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As the photo-dissociation product of methanol on the $\text{TiO}_2(110)$ surface, the diffusion and desorption processes of formaldehyde (HCHO) were investigated by using scanning tunneling microscope (STM) and density functional theory (DFT). The molecular-level images revealed the HCHO molecules could diffuse and desorb on the surface at 80 K under UV laser irradiation. The diffusion was found to be mediated by hydrogen adatoms nearby, which were produced from photodissociation of methanol. Diffusion of HCHO was significantly decreased when there was only one H adatom near the HCHO molecule. Furthermore, single HCHO molecule adsorbed on the bare $\text{TiO}_2(110)$ surface was quite stable, little photo-desorption was observed during laser irradiation. The mechanism of hydroxyl groups assisted diffusion of formaldehyde was also investigated using theoretical calculations.

Key words: Diffusion, Desorption, Formaldehyde, Scanning tunneling microscope

I. INTRODUCTION

The understanding of diffusion process on surfaces is important in surface physical and chemical processes, especially in heterogeneous catalysis. Because most of chemical reactions occur on active sites such as interface, steps, surface point defects [1–3]. Reactants and intermediates need to be close to those active sites by diffusion process, and the products also need to be carried away from the active positions to keep reacting. So the diffusion process should be a key step in actual reaction [4–5]. Sometimes reactivity could be related with diffusivity of reactants and intermediates. Therefore, the research of diffusion process on surface in fundamental level plays an important guidance to optimize catalyst.

Since water splitting in a photo-electrochemical cell was reported in 1972, titanium dioxide (TiO_2) has received extensive and increasing attention because of its potential applications in clean hydrogen production [6]. It has been reported that pure TiO_2 has weak catalytic activity for water splitting, and adding some methanol could increase the productivity of H_2 obviously [7]. As the most important intermediate product, formalde-

hyde (HCHO) acted a key role in this catalytic process. The research of HCHO diffusion on TiO_2 surface could contribute to the understanding of the effect of HCHO in O–H bond cleavage of water molecules.

The rutile $\text{TiO}_2(110)$ has become a well-studied model catalyst surface partly due to its stability [6, 8–12]. The surface consists of protruding two-coordinated bridging oxygen (O_{br}) rows and five-coordinated Ti ($\text{Ti}_{5\text{c}}$) rows running in the [001] direction. As a major surface point defect, O_{br} vacancies can be easily introduced by ultrahigh vacuum (UHV) annealing. In order to investigate the microstructure and fundamental chemical property of $\text{TiO}_2(110)$, high-resolution scanning tunneling microscope (STM) is performed to provide detailed information at submolecular level. STM studies have shown the surface structure [13, 14], molecular adsorption [15–20], metal-doping [21–25] and chemical reactions [26–28]. Furthermore, time-lapsed STM studies by Besenbacher *et al.* could record the fast changing of STM images as a STM movie, and they show a dramatic diffusion movie about ethanol diffusion along and across the Ti rows by assistant of hydrogen adsorbed on bridging bonded oxygen (BBO-H) [29].

Methanol photocatalysis has been studied on TiO_2 single crystal surface as well as on supported nanoparticles using various techniques [30–34] because adding methanol could dramatically enhance the water splitting efficiency which we mentioned before [7]. HCHO

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is always considered to be the key factor to accelerate the water splitting [35–37]. Meanwhile, HCHO could further react with another methoxy radical to form methyl formate [38, 39]. And chemical reaction of HCHO on TiO₂(110) has been extensively studied [40–43]. Recently, we reported a real-space imaging of a complete photocatalytic process for a single methanol on TiO₂(110) surface by direct high resolution STM imaging [44]. Photo-dissociation process can be followed step by step, and HCHO was resolved as a product by experimental imaging and theoretical simulation. Actually the evolution of images was due to the diffusion and desorption of HCHO. After the cleavage of both O–H and C–H bond on methanol molecular, HCHO was adsorbed on the original position. Then it tended to diffuse to the adjacent Ti site, and desorbed from the surface finally. This phenomenon reveals the diffusion of HCHO on the TiO₂(110) exists which is consistent with our previous conjecture.

In this work, we report all the transfer possibility including diffusion and desorption of HCHO on the surface under UV light irradiation by low-temperature STM and DFT calculation. The results indicated HCHO could diffuse both parallel and perpendicular to the rows of O_{br}. In contrast with other environments of HCHO's adsorption sites, HCHO presented different activity including diffusion and desorption. Possible reasons are discussed based on the energetic calculation, and the decrease of the diffused barrier is the key point of the whole complex phenomena.

II. EXPERIMENTS AND COMPUTATIONAL METHODS

The experiments were performed in a UHV chamber equipped with a low-temperature scanning tunneling microscope (LT-STM) (Matrix, Omicron). The vacuum in the STM chamber was maintained in UHV condition ($<4 \times 10^{-11}$ Torr). CH₃OH and HCHO were dosed on TiO₂(110) at 80 K, and the real space STM images were recorded at the same temperature. In this experiment, we always made a STM scan on the clean and the dosed CH₃OH and HCHO surface before each light irradiation period, and the STM tip is then pulled back by about 20 μm from the surface during CH₃OH and HCHO dosing and laser irradiation. After a laser irradiation period was completed, we then engaged the STM tip to the surface again and found the same surface area to trace the change of each individual molecule. The UV laser irradiation was accomplished by using a 355 nm ns-laser (HIPO, Spectra-Physics) in our photoreaction. The pulse duration is 12 ns, and the high frequency of 50 kHz could ensure that the surface was not damaged by this UV laser irradiation.

All the calculations were carried out with the Vienna *ab initio* simulation package (VASP) code [45, 46]. The generalized gradient approximation (GGA)

with the spin-polarized Perdew-Burke-Ernzerhof (PBE) functional [47] and plane augmented waves (PAW) potential [48] were used for characterize optimized molecular structures of TiO₂(110). The wave function was expanded by plane wave with kinetic cutoff of 400 eV and density cutoff of 650 eV. Our surface model was cut out of a six-layer slab TiO₂ crystal to expose the (110) surface [31, 49]. Monkhorst-Pack grid [50] of (2×1×2) *k*-points was used for the 4×2 surface unit cell. One HCHO was adsorbed on the top layer. All Ti_{5c} sites on the bottom layer were saturated with water molecules to maintain the bulk coordination environment [32]. Transition states were located by constrained minimization and climbing-image nudged elastic band methods [51, 52].

III. RESULTS AND DISCUSSION

A. HCHO adjacent to various numbers of H atom on TiO₂(110) surface at 80 K

FIG. 1(a) is a photo-reacted surface which was covered by methanol. The methanol was dosed at 80 K and irradiated by UV laser. The bright rows are due to the in-plane Ti_{5c} atom rows, and the dark rows are two-fold coordinated O_{br} atom rows. O_{br} vacancies show up as bright spots on the Ti_{5c} rows. Most of methanol adsorbed on the Ti_{5c} sites and two of them reacted after irradiation by 355 nm 50 mW ns-laser which is shown in FIG. 1(a). The O–H and one C–H bond on methyl cracked and the hydrogen atoms dropped on the adjacent O_{br} sites. The species of the big spot are one formaldehyde molecule on original adsorption site and two hydrogen atoms adsorbed on adjacent BBO sites. We reported that three distinct products formed in previous work, which represented reacted methanol and the following diffusion and desorption form, respectively [44]. Except the diffusion parallel to the Ti_{5c} rows we reported, another kind of diffusion was observed, which is shown in FIG. 1 (e) and (f). The HCHO crossed the O_{br} row and adsorbed on the neighbored Ti row which looks like “pole vault” with one hydrogen adatom, even the existence of BBO-H increased the height of jumping on topological structure. It is worth noting that these two types of diffusion correspond to the two dimension on the surface, so it means the formaldehyde can diffuse on the surface easily. We observed both the diffusions happened around the BBO-H and no one could diffuse further, which allows us to deduce the hydrogen atoms acted as a important role in the diffusion process. Double-irradiation experiment was also performed to measure the diffusion and desorption proportions. After the first irradiation, the elliptical spots which represent HCHO localized in the middle of two BBO-H atoms are marked. Then the system is illuminated again by 50 mW 355 nm laser for 10 min. Depending on the *in situ* photo reaction observation, the statistical results

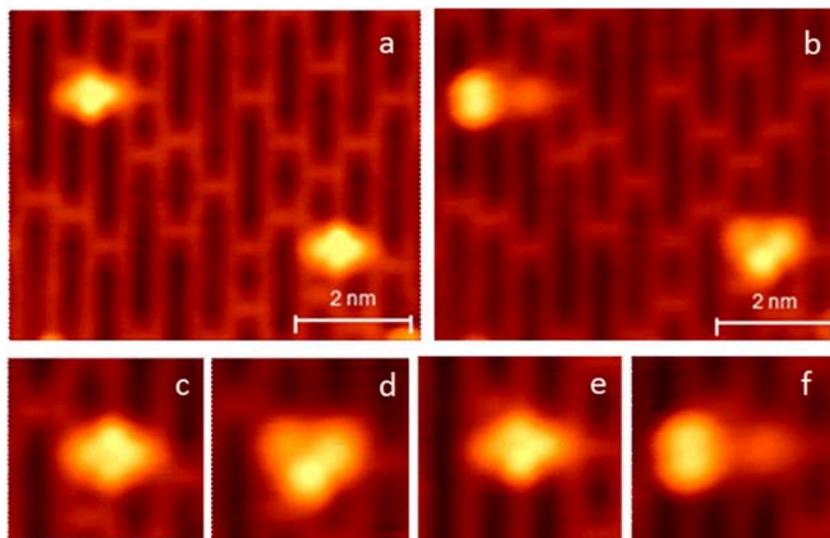


FIG. 1 The diffusion phenomena of the reacted methanol/TiO₂ surface. Every big protrusion in (a) consists of one HCHO molecule and two BBOH, and the HCHO molecule is localized between the two BBOHs. All of them are the products of photo-reacted methanol. (b) After second time of illumination, two kinds of diffusion could be observed. (c, e) Detailed images of both dissociated processes of methanols which are large versions of (a). (d, f) Detailed images of both diffusion processes of HCHO molecules which are large versions of (b).

TABLE I Statistical results of diffusion and desorption probability of HCHO adsorbed adjacent to 0, 1, and 2 BBO-H, respectively.

Compd.	Desorption	Diffusion	Total
Two-BBOH	16.1%(9/56)	28.5%(16/56)	44.6%
One-BBOH(h-TiO ₂)	5.6%(5/89)	6.7%(6/89)	12.3%
Zero-BBOH(r-TiO ₂)	3.1%(4/127)	0%(0/127)	3.1%

could be counted clearly which are shown in Table I. The proportions of diffusion and desorption are 16.1% and 28.5%, respectively.

As we know, the dissociation of methanol is a typical endothermic reaction, the energetics calculation indicated the reaction barrier is 1.6 eV and the energy difference between reactant and products is 1.1 eV [31]. This result suggested the energy of photon not only dissociated the methanol but also induced diffusion or desorption of HCHO. Proceeding from this perspective, the HCHO should be very active on Ti_{5c} sites. So it is meaningful to investigate binding energy and adsorption situation of HCHO on bare surface. Then the photo-induced diffusion and desorption experiment is performed by the same UV light. Surprisingly, the behavior of pure HCHO is very stable under the laser irradiation. The diffusion and desorption proportions are also listed in Table I which shows a significant difference from HCHO localized in-between two BBO-Hs. Only four HCHO molecules desorbed from the substrate and no one could diffuse to the adjacent Ti row or neighbored Ti site. The *in situ* desorption phenomenon is shown in FIG. 2. So we speculated that the two hydro-

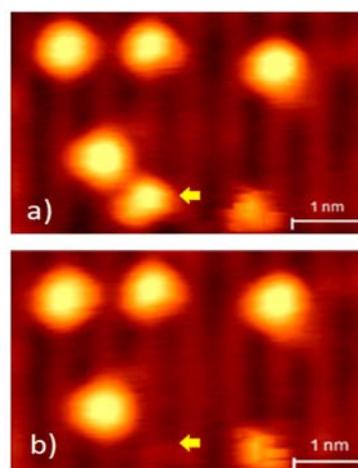


FIG. 2 Photo-desorption of HCHO on TiO₂(110). (a) HCHO adsorbed on the bare surface. (b) After laser irradiation, only rare desorption could be observed, which is marked by a yellow arrow.

gen adatoms induced the activity of HCHO.

To further prove this conjecture, we investigated the movement of HCHO which localized only one BBO-H. If surface hydroxyl could increase the activity of HCHO, the probability of diffusion and desorption should be located in between two statistical results. A special hydrated TiO₂(110) surface was prepared by dosing water at room temperature the photo-desorption are shown in FIG. 3(a) [14, 18], water only adsorbed on the vacancies and dissociated spontaneously. The brighter protrusions on the O_{br} rows are BBO-H atoms. The big-

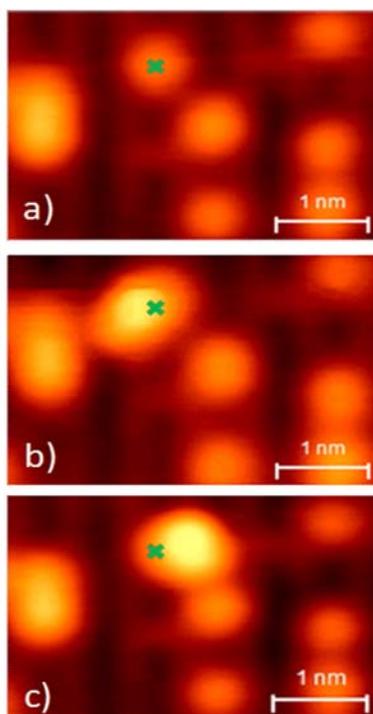


FIG. 3 The diffusion of HCHO with one BBO-H nearby on the hydrate- $\text{TiO}_2(110)$. (a) Hydrate- $\text{TiO}_2(110)$, a target BBO-H is marked by green \times . (b) After dosing HCHO molecules, one HCHO molecular was localized at the adjacent Ti site. (c) HCHO molecule diffused to the neighbored Ti row after laser irradiation.

ger spots on the surface are impurities to mark the *in situ* position. After HCHO was dosed on the Ti_{5c} site, we could observe some target molecules adsorbed adjacent to the BBO-H directly. We also manipulated some HCHO molecules which are near the hydrogen atoms move to the adjacent Ti_{5c} site in order to increase the sample size. After the same laser irradiation, the movement of HCHO appeared as we expected. It could cross the O_{br} row and localize just at the symmetrical position. And the probability of diffusion and desorption fall in between situations of no BBO-H and two BBO-Hs. Considering the assisted effect of BBO-H in other system [29], we believe that the hydrogen adatoms on the O_{br} could assist the diffusion of HCHO, even reduce the binding energy to make it easy to desorb from the surface.

B. Calculated HCHO diffusion assisted by H atom on $\text{TiO}_2(110)$ surface at 80 K

To understand how BBO-H atoms could assist the diffusion of HCHO, theoretical calculation has been carried out to investigate the role of BBO-H in HCHO diffusion. The optimized structures of adsorbed HCHO and transition states of diffusion are shown in FIG. 4. Three adsorption structures of HCHO and BBO-H

atoms are considered: (i) HCHO molecule adsorbs on the Ti_{5c} with no BBO-H atom nearby; (ii) HCHO molecule adsorbs on the Ti_{5c} with one BBO-H atom nearby; (iii) HCHO molecule adsorbs on the Ti_{5c} with two BBO-H atoms nearby, the adsorption energies of HCHO are 0.49, 0.51, and 0.45 eV, respectively. The interactions between oxygen atoms of HCHO and Ti_{5c} atoms are different because of the existence of BBO-H. Without BBO-H nearby, the $\text{Ti}-\text{OCH}_2$ distance is 2.28 Å. However, adding H atoms on the neighbored BBO sites increase the density of Ti_{5c} 's electron cloud, which leads to the change of $\text{Ti}-\text{OCH}_2$ distance. Thus, with one and two BBO-H atoms nearby, the $\text{Ti}-\text{OCH}_2$ distance stretches to 2.37 Å, which means the adsorption energy should be decreased. However, the adsorption energy of HCHO with one BBO-H atom nearby is bigger than the other two adsorption structures, and the adsorption energies for all the three structures are very similar by considering the effect of hydrogen bonding between HCHO molecule and BBO-H atoms. Without BBO-H atom nearby, only a weak BBO-H-CHO bond is formed, the length of the weak bond is 2.26 Å. With one or two BBO-H atoms nearby, the length of the weak hydrogen bond increases to 2.40 and 2.52 Å, respectively. However, with one BBO-H nearby, a strong hydrogen bonding is formed between the BBO-H and O atom of HCHO, the length is 2.36 Å. When the HCHO molecule adsorbs between two BBO-H atoms, this length decreases to 2.32 Å, the bonding energy is further strengthened. Due to a variety of interactions between HCHO and the substrate, the adsorption energy of HCHO does not decrease with increasing BBO-H atoms nearby.

Whereas, the diffusion barriers are significantly reduced along with the increase of BBO-H atoms. The presence of hydrogen bonding could assist HCHO to diffuse across the O_{br} row. As the number of BBO-H atoms increases from 0 to 2, the energy of diffusion barrier decreases from 0.43 eV to 0.29 eV. We calculated the transition-state structures of HCHO cross the O_{br} row as shown in FIG. 4 (a)–(c). When there is no BBO-H, only the weak BBO-H-CHO hydrogen bond exist, the distance is 2.64 Å. However, after forming real hydrogen bonding with BBO-H, the distance of BBOH- OCH_2 is 1.95 and 1.83 Å for one and two BBO-H, respectively. This is why diffusion is easier when H atoms are localized on the BBO sites. Therefore, the energetic results suggested HCHO is more active for the diffusion cross O_{br} row when it adsorbed adjacent to the BBO-H. And the desorption should be related to the diffusion process, because the adsorption energies are not much different. Due to the easy diffusion of HCHO with the BBO-H nearby, we speculate that the desorption process could happen in the position of the intermediate state. Direct desorption were still hard which need several bonds cleaving together, but on the intermediate state, the $\text{Ti}-\text{O}-\text{CH}_2$ already cracked, only bonding energy of BBOH- $\text{O}-\text{CH}_2$ should be overcome. This two-

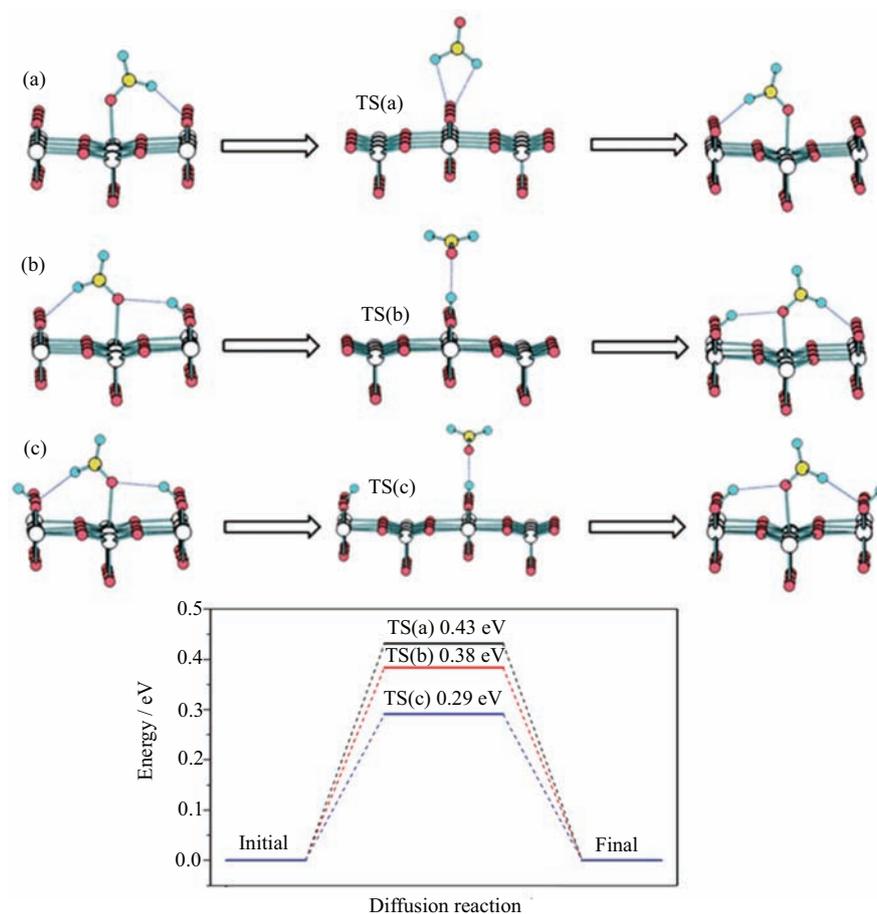


FIG. 4 Side view of HCHO via BBO diffusion reaction for the zero, one and two BBO-H cases are shown in (a)–(c), respectively. Transition states of diffusion are shown in TS(a), TS(b) and TS(c). The chart is the HCHO diffusion barriers with zero, one and two BBO-H, and shown by black, red and blue lines, respectively. Ti atoms are shown in white, O atoms are shown in red, C atoms are shown in yellow, and H atoms are shown in green. Blue dotted lines indicate hydrogen bonds.

step escape process from the surface should be reliable in energetics. Similarly, the diffusion as shown in FIG. 1(d) could be explained based on the similar two-step process. The HCHO in the immediate state did not escape from the surface or cross the BBO row, but fall down on the adjacent Ti_{5c} site. So we couldn't say the existence of BBO-H enhanced the probability of both diffusion and desorption generally, actually it reduced the difficulty of the diffusion and the diffusion is the precondition of desorption.

IV. CONCLUSION

In conclusion, we demonstrate a novel use of hydrogen atoms adsorbed on the BBO sites to investigate the strong assistant effect of a paralleled and perpendicular diffusion correspondent to BBO row. Both probabilities of diffusion and desorption increased continuously along with increasing of localized H atom on adjacent BBO sites. Theoretical calculations also proved this conclusion and further elucidated the relationship between

BBO-H and diffusion. Our results indicated BBO-H only increase the diffusion probability and the desorption should be the next step in the intermediate state of diffusion. This results proved the BBO-H species plays an important role in diffusion even chemical reactions.

V. ACKNOWLEDGMENTS

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