Role of Reduced Defects for Coupling Reactions of Acetaldehyde on Anatase TiO$_2$(001)-(1×4) Surface

Yuan-yuan Ji, Yi Zheng, Xiao-chuan Ma, Xue-feng Cui*, Bing Wang*

Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on January 28, 2019; Accepted on February 26, 2019)

The chemistry of acetaldehyde (CH$_3$CHO) adsorbed on the anatase TiO$_2$(001)-(1×4) surface has been investigated by temperature-programmed desorption (TPD) method. Our experimental results provide the direct evidence that the perfect lattice sites on the anatase TiO$_2$(001)-(1×4) surface are quite inert for the reaction of CH$_3$CHO, but the reduced defect sites on the surface are active for the thermally driven reductive carbon-carbon coupling reactions of CH$_3$CHO to produce 2-butanone and butene. We propose that the coupling reactions of CH$_3$CHO on the anatase TiO$_2$(001)-(1×4) surface should undergo through the adsorption of paired CH$_3$CHO molecules at the reduced defect sites, since the existing reduced Ti pairs provide the suitable adsorption sites.

Key words: Acetaldehyde, Coupling reaction, Reduced defect, Anatase TiO$_2$(001), Temperature-programmed desorption

I. INTRODUCTION

A carbon-carbon (C–C) coupling reaction is an important process for the conversion of biomass molecules to value-added chemicals [1–4], which commonly involves the key reaction step through the intermediate aldehydes [2]. As an important oxide support for metal catalysts [5], TiO$_2$ itself is a competent candidate (photo)catalyst for the C–C coupling reactions [6–10]. The C–C coupling reactions of aldehydes on TiO$_2$ have attracted wide study interests both experimentally and theoretically [11–24]. On both of the rutile TiO$_2$ and anatase TiO$_2$ surfaces, it is found that the existing surface defects are important for the C–C coupling reactions of acetaldehyde (CH$_3$CHO), which are consistent with the results for the reactions of other species at the defects [11, 25–34]. On the rutile TiO$_2$(110) surface [11, 15, 23] and the rutile TiO$_2$(001) surface [12–14], the C–C coupling reactions of CH$_3$CHO were observed. However, the reactions of CH$_3$CHO on anatase TiO$_2$ are seldom studied, and the roles of the defects on the reactions are less known at the atomic scale. The atomic geometries of the defects on the anatase TiO$_2$(001)-(1×4) surface were identified very recently [34], that is, the “TiO$_2$” vacancy, reduced Ti-rich defect, and partially oxidized Ti pairs in the ridges of the (1×4) reconstructed surface [26, 29, 30, 35].

In this work, we investigate the thermally driven reductive coupling reactions of CH$_3$CHO on anatase TiO$_2$(001)-(1×4) surface, using temperature-programmed desorption (TPD) method. The main product is 2-butanone, and the byproduct of butene is also observed. On the basis of the geometries of the identified defects, we can propose the C–C reaction route of CH$_3$CHO at the reduced defect sites of anatase TiO$_2$(001)-(1×4) surface.

II. EXPERIMENTS

All TPD experiments were carried out in an ultra-high vacuum (UHV) system with a base pressure below 2×10$^{-10}$ mbar. The desorption products were detected by a quadrupole mass spectrometer (QMS, MAX-120, Extrel) in the chamber, equipped with an Ar ion gun (ISE 5, Omicron) for sample treatment and a low-energy electron diffraction and Auger electron spectrometer (LEED/AES, SPECTALEED, Omicron) for analysis of surface elements and structure. The preparation of the anatase TiO$_2$(001)-(1×4) single crystal film was accomplished in another UHV multifunctional apparatus, consisting of a pulsed laser deposition (PLD) chamber (pressure of 1×10$^{-10}$ mbar), a scanning tunneling microscopy (STM) chamber (3×10$^{-11}$ mbar, Omicron) and an X-ray/ultraviolet photoemission spectroscopy (XPS/UPS) analysis chamber (8×10$^{-11}$ mbar, VG Scienta). The anatase TiO$_2$(001) sample was grown by means of PLD on a 0.7 wt% Nb-doped SrTiO$_3$(001) substrate, which was in O$_2$ atmosphere with pressure of 1.5×10$^{-5}$ mbar at 920 K during deposition. Details of the process of film growth have previously been described elsewhere [34, 36]. The as-grown surface was
transferred to TPD chamber under the protection of N2 and, for the resistive heating, was adhered to a Ta foil using high temperature ceramic adhesive (552, Aremco). A K-type thermal couple was glued on the sample surface to measure the temperature. The reduced surface was obtained by 1 keV Ar ion sputtering for 3 min and annealing in vacuum at 900 K for 20 min.

Acetaldehyde (Sigma-Aldrich, 99.5%) was purified by several cycles of “freeze-pump-thaw” process and then exposed to the sample at 100 K through a home-built doser, which was composed of a leak valve to control the gas flow and a tube of 4 mm in diameter to guide the gas to the surface. TPD spectra were measured at a fixedly ramping rate of 1 K/s with the sample directly facing the QMS.

III. RESULTS AND DISCUSSION

FIG. 1(a) shows a series of TPD spectra of the mass-to-charge ratio m/z=29 (CHO+) at various coverages exposures of CH3CHO on the as-grown anatase TiO2(001)-(1×4) surface, in which the surface is fully oxidized [34]. During the dosing of CH3CHO the substrate temperature was kept at 100 K. In the spectra, the red one is defined as 1 monolayer (ML, 1 ML=1.73×10^{-14} \text{ cm}^{-2}, with respect to the (1×4) unit cell), in which a nearly symmetric peak locates centered at about 210 K, and the 210 K adsorption state saturated while the shoulder peak from the adsorption of second layer was about to arise. The labeled coverages are obtained by integrating the area of each spectrum, with respect to the area of the defined spectrum of 1 ML. The features in the TPD spectra for CH3CHO are similar to the ones for CH2O [26], but a saturated desorption peak of the first layer (at 210 K) is observed for CH3CHO, different from the coverage-dependent signal for CH2O. FIG. 1(b) shows the TPD spectra of simultaneously recorded signals of 1 ML CH3CHO, in which only the signals from the molecular CH3CHO are observed. The results indicate that the as-grown surface, that is, the fully oxidized surface, is inert for the reaction of CH3CHO, which is consistent with the results of

DOI:10.1063/1674-0068/cjcp1901017
methanol [29].

FIG. 1 (c) and (d) shows the results from the reduced anatase TiO$_2$(001)-(1×4) surface. While the desorption of molecular CH$_3$CHO is observed at the low temperature range, similar to the as-grown surface, an additional peak centered at 400 K is observed. The various $m/z$ signals of the surface with 1.0 ML CH$_3$CHO are enlarged in the inset, which shows quite different relative intensities from the molecular CH$_3$CHO.

In previous studies, it was reported that the aldol condensation of CH$_3$CHO to produce crotonaldehyde and crotyl alcohol occurs on the oxidized rutile TiO$_2$(001) surface [12, 13], whereas the reductive coupling to produce butene occurs on the reduced rutile TiO$_2$(001) surface [14]. In the most studied rutile TiO$_2$(110) surface, the products of butene on reduced surface and acetate on oxidized surface [15] were also observed with the desorption of molecular CH$_3$CHO at low temperature range. In a recent work by Yang’s group, the important role of the bridging-bonded oxygen vacancies to produce 2-butanone and butene has been reported [11]. While most investigations of CH$_3$CHO adsorption on TiO$_2$ surfaces were based on rutile phase, only a small amount of experimental work was performed for aldehyde on anatase TiO$_2$ surfaces [16, 26]. Recently, TPD results of CH$_3$CHO on the anatase TiO$_2$(101) surface revealed that three main reaction products, 2-butanone, crotonaldehyde and crotyl alcohol, were observed without UV illumination, and the synthesis of 2-butanone via the coupling of CH$_3$CHO can be improved under UV light irradiation [16]. The anatase TiO$_2$ (001) surface was theoretically predicted to be more reactive than rutile surfaces [37-39], the mechanism of the C–C coupling reaction is far from well understood.

To identify the products for the observed peak at around 400 K. FIG. 2 shows the observable signals of $m/z=26$ (C$_2$H$_5^+$), 27 (C$_2$H$_3^+$), 29 (CHO$^+$), 41 (C$_4$H$_5^+$), 42 (C$_2$H$_2$O$^+$ and/or C$_3$H$_4^+$), 43 (C$_2$H$_3$O$^+$ and/or C$_3$H$_5^+$), 56 (C$_6$H$_7^+$), 57 (C$_5$H$_6$O$^+$ and/or C$_4$H$_8^+$) and 72 (C$_5$H$_4$O$^+$) at 1.0 ML coverage of CH$_3$CHO on reduced surface, exposed at 100 K. There are two obvious desorption peaks centered at 390 and 430 K, as marked by the dashed lines. The desorption peaks centered at 390 K include the fragments of $m/z=26, 27, 29, 42, 43, 56, 57$ and 72. The silence of the signal $m/z=31$ suggested that the desorption products are not crotyl alcohol or other alcohols [11]. Meanwhile, the signal of $m/z=70$ was not detected, which may exclude the possible product of crotonaldehyde through aldol condensation of CH$_3$CHO [12–14]. According to the NIST Chemistry WebBook [40], the product at 390 K can be assigned to the product of 2-butanone, which is similar to the reported product through a carbon–carbon coupling reaction on rutile TiO$_2$(110) surfaces [11] and anatase TiO$_2$(101) surfaces [16]. The peaks centered at 430 K therefore include the tiny contributions from fragments of $m/z=39, 41, and 56$, which can be assigned to the product of butene [41]. The product of butene was also observed in the C–C coupling reaction of acetaldehyde on other surfaces [11, 12], which are ascribed to the reductive coupling of CH$_3$CHO adsorbed at the defects of the reduced surface. Our results show that both products of 2-butanone and butene can be produced through the thermally driven reactions of CH$_3$CHO at the defect sites of the reduced anatase TiO$_2$(001)-(1×4) surface.

FIG. 3 shows the dependence of signals ($m/z=43$ and 39) on the CH$_3$CHO coverages and the different substrate treatments. It can be seen that the productions of 2-butanone and butene tend to be saturated when the CH$_3$CHO coverages are higher than about 0.5 ML, as shown in the insets of FIG. 3 (a) and (c). The saturation of the signals can be associated with the number of the specific active sites that the coupling reactions of CH$_3$CHO take place. In comparison, there is no detectable product from the coupling reactions on the as-grown surface. Therefore, we conclude that the re-

DOI:10.1063/1674-0068/cjcp1901017 ©2019 Chinese Physical Society
FIG. 3 TPD spectra of (a) $m/z=43$ ($C_2H_3O^+$) and (b) $m/z=39$ ($C_3H_7^+$) obtained at various CH$_3$CHO coverages on the reduced anatase TiO$_2$(001)-(1×4) surface. (c) $m/z=43$ ($C_2H_3O^+$) and (d) $m/z=39$ ($C_3H_7^+$) obtained after different substrate treatments, for the CH$_3$CHO coverage of 0.5 ML. The CH$_3$CHO molecules were exposed at 100 K. After about tens of cycles, the production of 2-butanone and butene occurring at 400 K tends to decrease (red lines in (c) and (d), without annealing to a high temperature of 850 K), but can be recovered after annealing to 850 K for 20 min (black lines in (c) and (d)). The insets in (a) and (c) correspond to the amplified signal of $m/z=43$ from 320 K to 500 K.

Reduced defects, that is, the reduced Ti-pair sites [34], can be the active sites for the coupling reactions, which is similar to the reactions of formaldehyde and methanol at the reduced defects of the anatase TiO$_2$(001)-(1×4) surface [26, 29, 30]. In our experiment, the concentration of the reduced defect sites is about 0.02–0.03 ML. According to the ionization cross sections of CH$_3$CHO [42] and 2-butanone [43] and the areas of $m/z=29$ at the CH$_3$CHO coverage of 1 ML in FIG. 1(c), we obtain that the production of 2-butanone is about 0.017 ML, well corresponding to the concentration of the reduced defect sites. Due to the tiny amount of butene and the less pronounced peak at 430 K, such an estimation for butene is not available, but it can be just seen that butene is a byproduct in comparison with the 2-butanone.

We also observed that after repeating measurements up to tens of cycles, the productions of 2-butanone and butene tend to decrease, as shown by the red lines in the TPD spectra in FIG. 3 (c) and (d). Note that in the TPD measurements, the samples were only heated to 700 K. We find that the decreased productions of 2-butanone and butene can be recovered after having the sample annealed at 850 K for 20 min.

On the basis of our observations, we suggest that the C–C coupling reactions of acetaldehyde should take place at the reduced defect sites. FIG. 4 shows the schematic drawing of the reaction routes to produce 2-butanone and butene. According to the identified reduced defect sites, there are a pair of four-fold coordinate Ti (Ti$_{4c}$) atoms in the (1×4) ridges [34], at which the adsorbed CH$_3$CHO pair should be responsible for the C–C coupling reaction (FIG. 4(a)). After the desorption of 2-butanone at 390 K (FIG. 4(b)) or the desorption of butene at 430 K (FIG. 4(c)), one O atom or two O atoms may be left on the surface and partially oxidize the Ti$_{4c}$ defect. This may explain the reduction of the activity of the surface after cycles of measurements. The procedure by annealing treatment of the surface up to 850 K for 20 min in UHV can lead to the desorption of the additional O atoms [34], and recover the reduction of the surface. In the route of butene production, leaving two O atoms may be less favored, leading to the formation of butene as a byproduct.
IV. CONCLUSION

In this work, we have conducted TPD experiments to study the chemistry of CH$_3$CHO on the anatase TiO$_2$(001) surface. The experimental results demonstrate that the perfect lattice sites of the surface are quite inert for the reaction of CH$_3$CHO, while the reduced defect sites are active for the C–C coupling reactions of CH$_3$CHO to form 2-butanone and butene products on the surface. Our findings provide an insightful understanding for the coupling reactions of CH$_3$CHO on the reduced anatase TiO$_2$(001) surface.

V. ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology of China (No.2016YFA0200603), the National Natural Science Foundation of China (No.91421313 and No.21573207), and Anhui Initiative in Quantum Information Technologies (AHY090300).

[23] J. J. Plata, V. Collico, A. M. Mrquez, and J. F. Sanz,
[40] https://webbook.nist.gov/cgi/cbook.cgi?ID=C78933&Units=SI&Mask=200
[41] https://webbook.nist.gov/cgi/cbook.cgi?ID=C624646&Units=SI&Mask=200