Acetone Formation from Photolysis of 2-Propanol on Anatase-TiO$_2$(101)

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Photocatalysis of 2-propanol on A-TiO$_2$(101) has been investigated using a temperature programmed desorption method with 266 nm laser light. A clear mechanism is proposed for photodissociation of 2-propanol on A-TiO$_2$(101). Acetone product on five coordinate Ti$^{4+}$ sites is formed in a stepwise manner in which the O–H dissociation proceeds first and then followed by secondary C–H dissociation of 2-propanol while H atoms are transferred to the adjacent bridge bond oxygen (BBO) sites. Low temperature water is formed in a thermally driven process via H-atom on BBO in exchange with isopropyl groups of molecule 2-propanol, while isopropyl radical desorbs at high temperature during the TPD process. The observation demonstrates the prospect of TiO$_2$ as a photocatalyst for degradation of organics.

Key words: 2-Propanol, Photochemistry, A-TiO$_2$(101), Temperature-programmed desorption

I. INTRODUCTION

Titanium dioxide (TiO$_2$) has been widely investigated as a photocatalyst in many important directions, including photocatalytic processes, heterogeneous catalysis chemical sensors, and environmental pollutants [1–5]. The potential use of TiO$_2$ for photocatalytic degradation of organic substances has attracted significant attention in recent years. TiO$_2$ exists in three polymorphs: rutile, anatase, and brookite [6]. Rutile and anatase are the most common crystal phases, while brookite will be transformed to rutile under high temperature. As the more active and popular form in actual photocatalytic application, anatase has not got plenty of researches in a single crystal level compared with rutile.

2-Propanol, along with other alcohols, is a major contaminant in indoor air and air streams. It is also an important surface probe for semiconductor metal oxide photocatalytic reactions [7–9]. In recent years, photochemistry of 2-propanol on TiO$_2$ [10–16] has been extensively studied as a model system on rutile(R)-TiO$_2$(110). Zdenek and coworkers [14] found that dehydration of 2-propanol to propene occurs on R-TiO$_2$(110). Zdenek and coworkers [14] found that dehydration of 2-propanol to propene occurs on R-TiO$_2$(110) at both low and high temperature. The low-temperature (300–450 K) channel is attributed to 2-propanol dehydration on the five coordinated Ti$^{4+}$ sites (Ti$_{5c}$). The high-temperature channel peak between 570 and 580 K is interpreted in terms of decomposition of 2-propoxy species formed by dissociative adsorption of 2-propanol on bridging oxygen vacancies. Later, David and coworkers [10] has investigated thermal and photocatalytic dehydrogenation of 2-propanol to acetone on the surface in the presence of molecular O$_2$. In the absence of light, the probability of producing either propene or acetone is small. However, upon band-to-band excitation with ultraviolet (UV) light irradiation, this probability of acetone production increases significantly, and the acetone production becomes the dominant reaction channel. The authors [10] also found that reductive surface is more active than oxide surface for the reaction. Not only O–H bond scission, C–C bond can also be broken during the photo-irradiation. Recent results obtained by Kershis and coworkers [17] using temperature programed desorption (TPD) and pump-probe laser ionization techniques have shown that methyl radicals are produced during the photocatalytic oxidation of 2-propanol on R-TiO$_2$(110). The result showed that the first step involves photocatalytic dehydrogenation to acetone intermediate, similar to previous studies [7, 10, 11]. Methyl radicals are ejected from the surface when the surface is irradiated with UV light. Furthermore, kinetic energy distributions of methyl radical are remarkably similar to those measured for the photooxidation of acetaldehyde and acetone [18, 19]. This result suggested that methyl radicals are produced during a second photocatalytic step which involves photooxidation of ketone intermediates. Even though a lot of photocatalysis studies have been carried out on R-TiO$_2$(110), very little has been done on well-defined anatase surfaces [20].

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In this work, we have investigated the photolysis of 2-propanol on anatase(A)-TiO$_2$(101) using TPD. Our results show that photoinduced acetone production on the five coordinate Ti$^{4+}$ (Ti$_{5c}$) sites occurs in a step-wise manner in which the O–H dissociation proceeds first and is then followed by secondary C–H dissociation of 2-propoxy. Low temperature H$_2$O is also detected due to the thermally driven process via H-atom on BBO in exchange with isopropyl groups of molecular 2-propanol, while isopropyl radicals desorb at high temperature during the TPD process.

II. EXPERIMENTAL METHOD

Photolysis of 2-propanol was carried out in an ultrahigh vacuum chamber with base pressure better than 4×10$^{-11}$ torr. TPD products were detected with a quadrupole mass spectrometer (Extrel), and the vacuum of the electron-impact ionization region was maintained at an extremely high vacuum of 1.5×10$^{-12}$ Torr. The ionization region [21] was housed in a liquid nitrogen cooled vacuum region that employed a 500 L/s turbo molecular pump. A liquid nitrogen cooling titanium sublimation pump was also used for this region. This low ambient pressure allows the measurement of TPD signals with very high sensitivity.

The A-TiO$_2$(101) crystal (Princeton Scientific Corp., 4 mm×4 mm×0.5 mm) was cleaned by cycles of Ar$^+$ sputtering and ultra-high vacuum (UHV) annealing at 800 K. To make sure that the surface was clean and well-ordered, Auger spectroscopy and low energy electron diffraction were characterized. 2-Propanol (Sigma-Aldrich, 99.5%) was purified by several freeze-pump-thaw cycles before use. 2-Propanol was dosed on the surface using a home-built, calibrated molecular beam doser, which has been described in detail elsewhere [22] at a surface temperature of 120 K. TPD measurements were carried out with a heating rate of 2 K/s.

Fourth harmonic (266 nm) output of a diode-pumped, solid state, Q-switched 1064 nm laser (Spectra-Physics) was used to induce the photochemistry of 2-propanol. The laser pulse duration was about 12 ns, and the laser repetition rate was 50 kHz. In order to minimize the temperature increase of the surface resulting from laser irradiation and to reduce surface damage by laser irradiation, only 5 mW of laser light was used to illuminate the 2-propanol covered A-TiO$_2$(101) surface. Laser beam diameter was ~3 mm, and its incident angle was ~30° with respect to the normal of the A-TiO$_2$(101) surface. Laser flux was thus 5×10$^{10}$ photons/(cm$^2$·s) for 266 nm.

III. RESULTS AND DISCUSSION

A. 2-Propanol TPD study on the A-TiO$_2$(101) surface

Figure 1 shows a series of TPD spectra collected at $m/z=45$ (C$_2$H$_5$O$^+$) as a function of 2-propanol exposure on the A-TiO$_2$(101) surfaces at 120 K. Between two TPD measurements, an UHV annealing at 800 K for 20 min was carried out to flat and clean the surface. The TPD spectrum of each exposure was reproducible for consecutive TPD experiments, indicating that the surface kept unchanged during the TPD process. Although TPD experiments of 2-propanol have been carried out on single rutile crystal surfaces and on anatase and rutile powders [10], the absolute coverages of 2-propanol on R-TiO$_2$(110) were determined using a combination of TPD and liquid nitrogen cooled quartz crystal microbalance measurements by Li and coworkers [23]. The saturation coverage of 2-propanol on the Ti$_{5c}$ sites of R-TiO$_2$(110) is about 0.61 ML, which is less than that of methanol on R-TiO$_2$(110). Li and coworkers [23] also suggested that the decrease of saturation coverage of 2-propanol on the Ti$_{5c}$ sites is attributed to additional steric hindrance that comes from increasing branching rather than length of the alkyl chains length. In this work, the absolute coverage of 2-propanol on A-TiO$_2$(101) is calibrated by a separate experiment of 2-propanol adsorption on R-TiO$_2$(110).

The TPD spectrum of the lowest coverage dosed on the surface, 0.11 ML (1 ML=5.2×10$^{14}$ molecules/cm$^2$), gives two peaks at about 345 and 620 K. The 345 K peak increases in intensity with increasing 2-propanol exposure (Fig.1) and shifts to 300 K when the exposure increases from 0.11 ML to 0.61 ML. Assignments of these TPD features will be discussed below in detail. The peak at 345 K is assigned to the desorption of molecular 2-propanol from the Ti$_{5c}$ sites. Compared with the result obtained on R-TiO$_2$(110), the desorption temperature of 2-propanol on A-TiO$_2$(101) is a little higher. This may be due to the larger distance of adjacent Ti$_{5c}$ sites on A-TiO$_2$(101), leading to the less salient steric-hinderance effect. When the first layer desorption peak is saturated on anatase TiO$_2$(101), the coverage of 2-propanol is nearly equal to 0.61 ML. So we speculated that saturation adsorption for 2-propanol...
on anatase TiO$_2$(101) is also 0.61 ML. Based on the similar adsorption behavior for CH$_3$OH and H$_2$O on A-TiO$_2$(101) [24], the 200 K peak may be attributed to the second layer 2-propanol adsorption on the two coordinated O$^{2+}$ sites (O$_{2c}$) with hydrogen bonds.

As the coverage of 2-propanol increases, both the intensity and desorption temperature of 620 K TPD peak change little (Fig.1), which is likely due to isopropoxy ((CH$_3$)$_2$CHO) reaction at the Ti$^{5c}$ sites. Due to the small signals of the TPD traces, it is very difficult to assign the products at the 620 K. Based on the reaction pathway detected in thermal decomposition of titanium tetraisopropoxide (Ti(OC$_3$H$_7$)$_4$) on Si(100) [25], the isopropoxy ligands adsorbed on the Si(100) surface undergo certain reactions to produce isopropanol, acetone, and propylene in the range of 350–700 K. The detected species in the wide temperature range from 550 K to 700 K (Fig.2) may be 2-propanol, acetone, and propylene produced from isopropoxy ((CH$_3$)$_2$CHO) reactions. However, no signal is observed at m/z=58, suggesting that acetone is not formed (Fig.2). Thus, we proposed that part of 2-propanol dissociatively adsorb at the Ti$^{5c}$ sites to form isopropoxy radicals and H atoms on the bridging bonded oxygen atoms (O$_{BBO}$) (H-O$_{BBO}$), similar to the methanol adsorption on the surface [20], and then isopropoxy radicals are disproportionated to produce propylene and 2-propanol with O atoms left on the Ti$^{5c}$ sites, rather than disproportionated to being acetone and 2-propanol.

\[
(\text{CH}_3)_2\text{CHO}(\text{Ti}^{5c}) \xrightarrow{\text{A-TiO}_2(101)} (\text{CH}_3)_2\text{CHO( Ti}^{5c}) + \text{H-O}_{BBO} \quad (1)
\]

\[
2(\text{CH}_3)_2\text{CHO( Ti}^{5c}) \xrightarrow{\text{Heat}} (\text{CH}_3)\text{CH=CH}_2(\text{gas}) + (\text{CH}_3)_2\text{CHO(gas)} + \text{O(Ti}^{5c}) \quad (2)
\]

Based on previous studies by Setvin and coworkers [26], the remaining O adatoms would react with subsurface oxygen vacancy to produce an interstitial (O$_2$)$_O$ species during the TPD process.

B. Photocatalysis of 2-propanol TPD study on the A-TiO$_2$(101) surface

Figure 2 shows TPD spectra acquired at m/z=15 (CH$_3$), 18 (H$_2$O$^+$), 27 (C$_2$H$_5$), 39 (C$_3$H$_7$), 41 (C$_3$H$_9$), 43 (C$_3$H$_{11}$), 45 (C$_3$H$_{13}$), 58 (C$_3$H$_{15}$O$^+$) after the adsorption of 0.4 ML of 2-propanol on the A-TiO$_2$(101) surface at 120 K (dashed lines), after 20 min irradiation time with a photon flux of $5\times10^{16}$ photons/(cm$^2$·s) (solid lines).

![FIG. 2 TPD spectra acquired at m/z=15 (CH$_3$), 18 (H$_2$O$^+$), 27 (C$_2$H$_5$), 39 (C$_3$H$_7$), 41 (C$_3$H$_9$), 43 (C$_3$H$_{11}$), 45 (C$_3$H$_{13}$), 58 (C$_3$H$_{15}$O$^+$) after the adsorption of 0.4 ML of 2-propanol on the A-TiO$_2$(101) surface at 120 K (dashed lines), after 20 min irradiation time with a photon flux of $5\times10^{16}$ photons/(cm$^2$·s) (solid lines).]

is from further reaction of isopropoxy. Taking into account of the 27 (C$_2$H$_5$), 39 (C$_3$H$_7$), 41 (C$_3$H$_9$), 43 (C$_3$H$_{11}$) TPD traces, the 450 K desorption peak is assigned to isopropyl radical desorption. After irradiation, a new peak appears at 270 K (m/z=15 (CH$_3$), 43 (C$_3$H$_{11}$), and 58 (C$_3$H$_{15}$O$^+$), indicating that new species is formed during UV irradiation, and the adsorption of the species on the surface is less stable than 2-propanol. Combination with additional TPD traces, the 270 K shoulder is assigned to acetone desorption from the Ti$^{5c}$ sites. In addition, isopropyl radical and low temperature H$_2$O signals also increase after irradiation.

To figure out the mechanism of 2-propanol photolysis on A-TiO$_2$(101), systematic study on the photocatalysis of 2-propanol has been carried out on the A-TiO$_2$(101) surface using 266 nm light with different irradiation times. As shown in Fig.3(a), the 300 K TPD peak of m/z=45 (C$_2$H$_5$O$^+$), which is assigned to parent 2-propanol desorption from the Ti$^{5c}$ sites, decreases with increasing irradiation time, suggesting that 2-propanol is photo-dissociated to form acetone product or photo-desorbed during irradiation. Before irradiation, the signal profile of the 300 K peak from
0.61 ML of 2-propanol were dosed to the A-TiO$_2$(101) surface at 120 K. (a) TPD spectra collected at $m/z=45$ ($C_2H_5O^+$) as a function of irradiation time with a photon flux of $5 \times 10^{16}$ photons/(cm$^2$s). $C_2H_5O^+$ is mainly formed by dissociative ionization of desorbed parent 2-propanol in electron-bombardment ionizer. (b) TPD spectra collected at $m/z=43$ ($C_3H_7^+$) as a function of irradiation time. $m/z=43$ was exactly the same as that from $m/z=45$, indicating that this peak was the result of dissociative ionization of the desorbed parent 2-propanol molecule in the electron-bombardment ionizer. Acetone product increases remarkably with increasing irradiation time. The fact that the 620 K peak in $m/z=45$ TPD decreases rapidly after 1 min irradiation implies that isopropoxy has a much higher reactivity than molecular 2-propanol (Fig.3). This is consistent with previous study by Xu and coworkers [20] on A-TiO$_2$(101) that methoxy has a much higher reactivity than molecular methanol, further indicating that product acetone can be produced from isopropoxy dissociation. Photochemistry of alcohols especially methanol on R-TiO$_2$(101) [28] and A-TiO$_2$(101) [20] have been well studied by Guo and coworkers. Stepwise photocatalytic dissociation of methanol existed on both two surfaces. Considering the fact that part of 2-propanol molecules dissociatively adsorb at the Ti$_{5c}$ sites to produce isopropoxy and H–O$_{BBO}$, and isopropoxy radicals dissociate to form acetone during irradiation, acetone formation occurs via transferring the hydroxyl hydrogen of 2-propanol to the O$_{BBO}$ sites nearby to form isopropoxy.

$\text{(CH}_3\text{)}_2\text{CHOH(Ti}_{5c}\text{)} \xrightarrow{\text{hv or heat}} \text{(CH}_3\text{)}_2\text{CHO(Ti}_{5c}\text{)} + \text{H–O}_{BBO}$ (3)

$\text{(CH}_3\text{)}_2\text{CHO(Ti}_{5c}\text{)} \xrightarrow{\text{hv}} \text{(CH}_3\text{)}_2\text{CO(Ti}_{5c}\text{)} + \text{H–O}_{BBO}$ (4)

In order to detect dissociated H atoms from photolysis of 2-propanol on the A-TiO$_2$(101) surface, relevant masses of TPD have been measured. Without irradiation, a broad peak at $m/z=45$ is observed near 260 K (Fig.4). According to a previous report [24], this peak is assigned to molecule H$_2$O desorption from the Ti$_{5c}$ sites. No H$_2$O desorption at high temperature indicates that little defects exist on the surface. A recent study [29] showed that only about 0.005 ML of point defects on the A-TiO$_2$(101) surface can be formed via UHV annealing. The amount of H$_2$O before irradiation is about 0.05 ML, which is account for 9% of the proportion of parent 2-propanol. This cannot be due to the impurity of H$_2$O in 2-propanol, which is less than 0.5% as the gauged by the mass spectrometry of 2-propanol. Based on our previous experimental study for photochemistry of methanol on A-TiO$_2$(101) [20], the low temperature H$_2$O can be produced through two steps. First, part of methanol molecules dissociatively adsorb at the Ti$_{5c}$ sites to form methoxy radicals and H–O$_{BBO}$ atoms,

$\text{CH}_3\text{OH(Ti}_{5c}\text{)} + \text{O}_{BBO} \xrightarrow{\text{A-TiO}_2(101)} \text{CH}_3\text{O(Ti}_{5c}\text{)} + \text{H–O}_{BBO}$ (5)
FIG. 5 Yields of H$_2$O and isopropyl radical (C$_3$H$_7^+$) as a function of laser irradiation time.

And then, exchange reaction occurs to produce H$_2$O on the Ti$_{5c}$ sites during the TPD process,

$$\text{CH}_3\text{OH}(\text{Ti}_{5c}) + \text{H} \rightarrow \text{H}_2\text{O}(\text{Ti}_{5c}) + \text{CH}_3\text{O}$$  

Here, the low temperature H$_2$O may be also due to the exchange reaction during the TPD process,

$$\text{(CH}_3\text{)}_2\text{CHOH(Ti}_{5c}) + \text{H} \rightarrow \text{H}_2\text{O(Ti}_{5c}) + \text{(CH}_3\text{)}_2\text{CH} - \text{O}$$  

Correspondingly, the coverage of isopropoxy ((CH$_3$)$_2$CHO) formed via spontaneous 2-propanol dissociation at the Ti$_{5c}$ sites can be estimated to be 0.05 ML. Integrated signals of products H$_2$O and isopropyl radical are shown in Fig.5. While, concomitant to the increase of H$_2$O after irradiation, isopropyl radicals have the same growth trend, which is consistent with our previous studies of methanol dissociation on the surface that thermally driven exchange reaction occurs to produce H$_2$O molecules at the Ti$_{5c}$ sites and methyl radicals on the O$_{BBO}$ sites [20].

Figure 6 shows the yield of H$_2$O and depletion of parent 2-propanol as a function of laser irradiation time. Without irradiation, 0.05 ML H$_2$O is generated by thermally driven exchange reaction (Eq.(7)). The yield of H$_2$O production reaches a maximum after 40 min laser irradiation, which is possibly due to the increased hydrogen atoms on the bridge bond oxygen rows. Similar inhibiting effect has also been observed for photochemistry of methanol on R-TiO$_2$(110) [28].

As shown in Fig.6, 0.16 ML of 2-propanol is consumed and only 0.08 ML of H$_2$O is produced after 40 min irradiation, indicating that part of 2-propanol is photodesorbed during irradiation, or not all H atoms is converted to H$_2$O. There are two other possible reaction channels for the depletion of dissociated H atoms during the TPD process. First, due to the high background of H$_2$ in the ionization region, the detection of H$_2$ is very difficult, leading to no detection of this product. Second, the dissociated H atoms may diffuse into bulk during the TPD process. Corresponding theoretical studies [30] show that the diffuse of H$_2$O$_2$ atoms on A-TiO$_2$(101) into the bulk is at least equally favorable as desorbing in H$_2$ molecule form since this is both kinetically and thermodynamically favorable.

IV. CONCLUSION

UV photocatalysis of 2-propanol on the well-defined A-TiO$_2$(101) surface has been investigated using TPD method. Experimental results show that acetone product on the Ti$_{5c}$ sites is formed in a stepwise manner in which the O–H dissociation proceeds first and is then followed by secondary C–H dissociation of 2-propanol. Low temperature H$_2$O is formed exchange of H–O$_{BBO}$ atoms and isopropyl groups of molecular 2-propanol on the Ti$_{5c}$ sites, and isopropyl radicals desorb at high temperature.

This study clarifies the mechanism of photo-dissociation of 2-propanol on the A-TiO$_2$(101) surface. The observation further demonstrates the prospect of TiO$_2$ as a photocatalyst for degradation of organics.

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