

Room-temperature-adsorption behavior of acetic anhydride on a $\text{TiO}_2(110)$ surface

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Abstract

We have studied the adsorption structure of acetic anhydride on a $\text{TiO}_2(110)$ surface using XPS (X-ray photoelectron spectroscopy), LEED (low energy electron diffraction) and HREELS (high resolution electron energy loss spectroscopy) to determine the origins of the unique adsorption properties of carboxylic acids on a $\text{TiO}_2(110)$ surface. The C 1s XPS data indicated that the saturation carbon amount of adsorbed acetic anhydride was $12 \pm 3\%$ larger than that of the adsorbed acetic acid. LEED showed $p(2 \times 1)$ weak spots for the acetic anhydride adsorbed surface. The HREELS spectra revealed the dissociative adsorption of acetic anhydride. Based on these findings, we concluded that the neutralization of the bridging oxygen atoms associated with the dissociative adsorption is necessary for the stable adsorption of carboxylates on the 5-fold Ti sites.

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1. Introduction

A rutile $\text{TiO}_2(110)$ surface is the most intensively investigated single crystal oxide surface because of the interesting behavior of TiO_2 and its use in various applications including as catalyst [1], catalyst supports [2], chemical sensors [3,4], photocatalysts [5], bio-compatible materials [6–9], pigments [10]. Consequently, detailed physical and chemical properties of $\text{TiO}_2(110)$ surfaces have been unveiled and are available [11].

The adsorption of organic molecules on $\text{TiO}_2(110)$ is of importance, in order to understand catalysis behavior and dye function as well as to construct new nanomaterials. Table 1 summarizes the adsorption ability of some typical organic molecules on a clean $\text{TiO}_2(110)$ surface at room temperature [12–15]. Many organic compounds do not adsorb on the ideal $\text{TiO}_2(110)$ surface in a stable manner at

room temperature under UHV conditions. Most of them are stably present on the bridging oxygen defect site (O_B defect shown in Fig. 1). Only carboxylic acids adsorb stably to yield (2×1) long-range order structure as depicted in Fig. 2 [16–27]. The carboxylic acids dissociatively adsorb on a $\text{TiO}_2(110)$ terrace at room temperature and form carboxylates (RCOO^-) bound to two five-coordinate Ti^{4+} cations (denoted as Ti(5)) in a bridging form. The (OCO) plane is aligned parallel to the $\langle 001 \rangle$ axis. The saturation coverage is 0.5 ML (ML = monolayer) where 1 ML is equivalent to the exposed Ti(5) sites and the surface provides a well ordered $p(2 \times 1)$ periodicity in LEED and STM. The liberated protons are bound to bridging oxygen atoms (denoted by O_B , in Fig. 1) forming OH species [28–30]. The $\text{TiO}_2(110)$ surface seems to behave as if it were a basic oxide, and the adsorption of carboxylic acids can be rationalized by a neutralization reaction. Theoretical studies have indicated that the co-adsorbed proton on O_B plays an important role for the stabilization of carboxylates [29–32].

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Table 1

A brief summary of the adsorption behavior of organic molecules on a $\text{TiO}_2(110)$ surface at room temperature

Molecules	Molecule/Ti(5) ^a	Adsorption site	LEED	References
R-COOH	0.5	Ti(5) ^a	$p(2 \times 1)$	[11]
R-OH	Negligible	O_B defects ^a	None	[12,13]
R-CHO	Negligible	O_B defects ^a	–	[14]
Pyridine	Negligible	–	–	[15]
Benzene	Negligible	–	–	[15]

^a See Fig. 1 as references of the abbreviations.

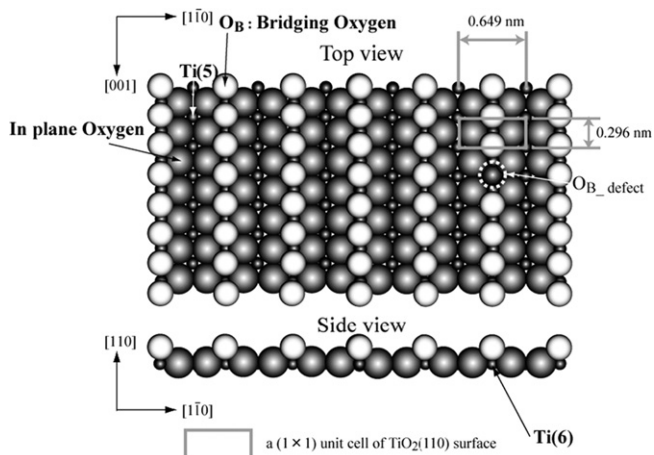


Fig. 1. A ball stick model of the $\text{TiO}_2(110)$ surface.

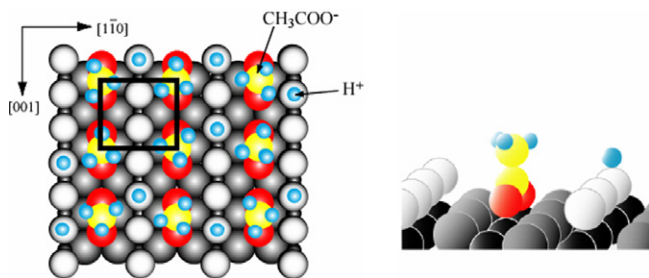
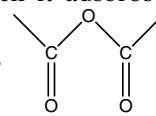


Fig. 2. A $p(2 \times 1)$ adsorption structure of AcOH on $\text{TiO}_2(110)$.

However, there is another possibility for the origin of the stable adsorption of carboxylic acid on a $\text{TiO}_2(110)$ surface. Carboxylates are bidentate and can coordinate to the two exposed Ti(5) atoms of the $\text{TiO}_2(110)$ surface as a bridging form, as shown in Fig. 2. Bates et al. pointed out that the formate in a bridging form gains significant adsorption energy [29]. They claimed that the bridging geometry preserved the symmetry necessary for resonant stabilization as compared to a unidentate formate. In order to experimentally answer the fundamental question about why carboxylates adsorb stably on a $\text{TiO}_2(110)$ surface and form the long-range order, we chose acetic anhydride as a test molecule. Acetic anhydride does not have any proton. Instead it has two carbonyl groups which have a

nearly coplanar molecular structure so that it gains resonant stabilization energy when it adsorbs molecularly to

the two Ti(5) atoms with its



plane parallel

to the [001] direction. In addition, the distance between two C=O bonds (0.265 nm) is somewhat shorter than the surface Ti(5)–Ti(5) distance (0.296 nm) and a little longer than the O–O distance in the formate ion (0.2355 nm). Therefore, if the latter hypothesis were correct, a remarkable amount of acetic anhydride could molecularly adsorb on the $\text{TiO}_2(110)$ surface in a stable manner. In this paper, we report a study on the adsorption structure of acetic anhydride on a $\text{TiO}_2(110)$ surface by means of XPS, LEED and HREELS to reveal the origin of the adsorption property of carboxylates.

2. Experimental

All measurements were carried out in a UHV measurement chamber (base pressure: 3×10^{-8} Pa) equipped with a high resolution electron energy loss spectrometer (HREELS) (ELS-3000, LK technology, USA), a micro-channel plate low energy electron diffraction optics (LEED) (BDL-800IR-MCP, OCI Vacuum Microengineering, Canada) and an X-ray photoemission spectrometer (XPS) (VG100AX, Thermo Electron Corporation, UK, Mg $K\alpha$, 13 kV–13 mA, Pass energy = 50 eV). All HREELS spectra were collected in the specular direction with an incident electron beam direction of 60° from the surface normal. The primary electron energy was 6.3 eV. The typical peak intensity and full width at half maximum (FWHM) of the elastic peak on the molecule-adsorbed $\text{TiO}_2(110)$ surface were 30,000 counts/s and $21\text{--}24 \text{ cm}^{-1}$, respectively. The LEED optics has a micro-channel plate which allows for low electron current experiments to minimize sample damage during LEED observations. The typical beam current was 1.0 μA . An optically polished rutile $\text{TiO}_2(110)$ single crystal sample ($10 \times 10 \times 0.5 \text{ mm}^3$, Furuuchi Co., Japan) was pretreated at 1273 K for 3 h in air and then loaded in the UHV preparation chamber (base pressure 3×10^{-8} Pa). The sample was cleaned by cycles of 3 keV Ar^+ sputtering and annealed at a temperature of 1000 K. These procedures yielded a sharp (1×1) LEED pattern (Fig. 6a) and little C 1s contamination on the $\text{TiO}_2(110)$ surface.

Acetic acid (AcOH) and acetic anhydride (Ac_2O) (Wako Co., Japan) were purified by several freeze–pump–thaw cycles and their purities were checked using a quadrupole mass spectrometer (M-200QA, ANELVA, Japan). They were adsorbed on cleaned $\text{TiO}_2(110)$ surfaces at room temperature (RT) by backfilling the chamber from a metal leak release valve under dynamic pumping with a turbo-molecular pump. The AcOH and Ac_2O doses were carried out at 10^{-5} Pa. Since the ionization gauge was at a distance from the sample and close to the turbo-pump, we might have

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