



Effects of the crystal reduction state on the interaction of oxygen with rutile $\text{TiO}_2(1\ 1\ 0)$

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ABSTRACT

The interaction of O_2 with reduced rutile $\text{TiO}_2(1\ 1\ 0)-(1 \times 1)$ has been studied by means of scanning tunneling microscopy (STM), temperature-programmed desorption (TPD) and photoelectron spectroscopy (PES). It is found that the interaction of O_2 with $\text{TiO}_2(1\ 1\ 0)$ depends strongly on the reduction state of the $\text{TiO}_2(1\ 1\ 0)$ crystal. High-resolution STM studies revealed that the energy barrier for the non-vacancy-assisted, 2nd O_2 dissociation channel decreases with increasing crystal reduction. Additionally, it is found in the STM studies that the Ti interstitial diffusion is slightly more facile in high-reduced $\text{TiO}_2(1\ 1\ 0)$ crystals compared to low-reduced ones. Accompanying TPD studies revealed that the line shape of the O_2 -TPD peak occurring between $\sim 360\ \text{K}$ and $\sim 450\ \text{K}$ depends on the crystal reduction state. For high-reduced $\text{TiO}_2(1\ 1\ 0)$ crystals characterized by large terraces most O_2 molecules desorb at $\sim 386\ \text{K}$, whereas O_2 desorption is peaking at $\sim 410\ \text{K}$ for low- and medium-reduced crystals. Furthermore, the O_2 -TPD experiments revealed a highly non-linear behavior of the O_2 desorption peak integrals as function of the crystal reduction state. The presented results point to an ionosorption model where the adsorbates withdraw the excess charge (Ti^{3+}) from the near-surface region at temperatures $< \sim 360\ \text{K}$ and where Ti interstitials react with oxygen species on the surface at temperatures $\geq \sim 360\ \text{K}$.

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1. Introduction

Titanium dioxide (TiO_2) is used in a wide number of technological fields such as photocatalysis, heterogeneous catalysis, biocompatible materials, photovoltaic cells and gas sensors [1–9]. In all these applications the interaction of O_2 with TiO_2 plays an important role. For example, O_2 is a common oxidant and is used in photocatalysis as a scavenger of the photoexcited electrons to prevent negative charge accumulation on the surface of the catalysts [1,2,5,9]. Thus, to enhance the efficiencies in the current and future applications of TiO_2 it is essential to improve our fundamental understanding of how O_2 interacts with TiO_2 surfaces.

It is generally accepted that adsorbed O_2 species acquire negative charge upon adsorption on TiO_2 surfaces [7,9–18]. Theoretical calculations have shown that excess charge can be donated by all the various defects that are associated with Ti^{3+} such as O vacancies, surplus H and interstitial Ti [12,14,15,18–24]. The Ti^{3+}

excess electrons populate the normally empty Ti 3d orbitals on cations in the near and far proximity of the structural defects, leading to a state in the $\sim 3.1\ \text{eV}$ wide band gap [4,10,13,25–29]. It is this excess charge that can be donated to O_2 species on the TiO_2 surface [4,7,9–13,15–18,26,27,30,31]. However, which particular structural defects provide most of the Ti^{3+} excess electrons and are thus most relevant for the O_2 - TiO_2 interaction is today still unsettled [9,17,30,32].

To disentangle the contributions of the individual defects for chemical reactions on TiO_2 , the surface science approach [33] is most promising. For surface science studies addressing TiO_2 , the rutile $\text{TiO}_2(1\ 1\ 0)-(1 \times 1)$ surface has been often preferred (Fig. 1) [4,7,17,32,34,35]. Upon $\text{TiO}_2(1\ 1\ 0)$ sample preparation in ultrahigh vacuum (UHV), the crystals are reduced, leading to the creation of bulk defects such as Ti interstitials and bridging O (O_{br}) vacancies on the surface [4,13,35,36]. Considering that scanning tunneling microscopy (STM) studies addressing the anatase $\text{TiO}_2(101)$ surface revealed the absence of surface O vacancies [37], the formation of surface O vacancies in UHV may be a peculiar feature of rutile crystals.

The interaction of O_2 with rutile $\text{TiO}_2(1\ 1\ 0)$ has been studied previously using STM [4,13,17,30,32,35,38–49], temperature

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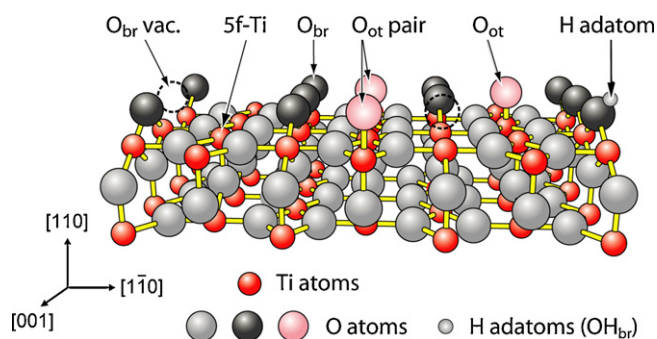


Fig. 1. (a) Ball-and-stick model of the rutile $\text{TiO}_2(110)-(1 \times 1)$ surface with O_{br} vacancies, H adatoms (OH_{br}), and single as well as paired O_{ot} adatoms. Large dark gray balls represent twofold coordinated O_{br} atoms, large light gray balls threefold coordinated O atoms and large pink balls O_{ot} adatoms. Small red balls represent Ti atoms and light gray balls H adatoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

programmed desorption (TPD) [10,11,30,49–52], photoelectron spectroscopy (PES) [13,25–27,53] and photon- or electron-stimulated desorption (PSD, ESD) [7,11,16,31,45,52,54–59]. At low temperatures (LT), that is for $110\text{ K} \leq T \leq 150\text{ K}$, O_2 molecules adsorb both molecularly and dissociatively on rutile $\text{TiO}_2(110)$ [13,30,41,45], whereas at room temperature (RT) dissociative adsorption is prevalent in low-pressure-experiments performed under UHV conditions [10,13,30,44]. Two different dissociative adsorption channels have been identified at RT: The 1st channel that is associated with O_{br} vacancy sites and the 2nd channel that occurs directly in the Ti troughs and is not associated with O_{br} vacancy sites [13,30,44]. As a result of dissociative O_2 adsorption, O adatoms are created that reside on-top on the 5f-Ti sites (O_{ot} adatoms, cf. Fig. 1). In the STM images, the O_{ot} adatoms appear as bright protrusions in the Ti troughs, rendering STM as the technique of choice for studying the dissociative adsorption of O_2 on $\text{TiO}_2(110)$.

Recent low-temperature STM studies [46–48] confirmed the occurrence of molecular and dissociative adsorption of O_2 , and also the existence of two O_2 dissociation channels has been confirmed by Wang et al. [47]. However, uncertainty still exists with regard to the temperatures at which the two O_2 dissociation channels set in. Whereas we found the onset of the 1st O_2 dissociation channel to occur at 110–130 K [13,41], Tan et al. [48] reported evidence for nondissociated O_2 at O_{br} vacancies at 130 K, and Wang et al. [47] reported that O_2 molecules would dissociate only for temperatures higher than 150 K.

Regarding the role of defects for the interaction of O_2 with rutile $\text{TiO}_2(110)$, Petrik et al. claimed that the amount of chemisorbed O_2 on TiO_2 depends mainly on the density of surface defects such as O_{br} vacancies and capping H adatoms [H_{ad} species, also known as bridging hydroxyl (OH_{br}) groups] [31]. These authors inferred that the Ti^{3+} excess charge associated with O_{br} vacancies and H_{ad} species rather than the charge provided from subsurface defects, such as Ti interstitials, determines the oxygen chemistry on rutile $\text{TiO}_2(110)-(1 \times 1)$ [31]. The same group also suggested that the excess charge associated with the 2nd, non-vacancy-assisted O_2 dissociation channel would stem predominantly from O_{br} vacancies [44] rather than from Ti interstitials as we proposed earlier [13]. Recently, we have provided further evidence that the adsorption of oxygen species on clean, reduced $\text{TiO}_2(110)$ surfaces is governed by the available Ti^{3+} excess charge in the near-surface region [30,49]. Specifically, we proposed that the desorption of O_2 molecules at $\sim 410\text{ K}$ is caused by a depletion of Ti^{3+} excess charge in the near-surface region induced by reactions between oxygen species and out-diffusing Ti interstitials [30]. These observations point to an ionosorption model for understanding redox processes

on the surface of reduced $\text{TiO}_2(110)$ rather than to charge donation from surface defects.

In the present article, we studied the interaction of O_2 with reduced $\text{TiO}_2(110)-(1 \times 1)$ surfaces for a wide range of crystal reduction states. We report on a strong influence of the crystal reduction state on the O_2 adsorption. An upper limit exists for the coverage of O_{ot} adatoms that can be adsorbed on $\text{TiO}_2(110)$. On high-reduced $\text{TiO}_2(110)-(1 \times 1)$ surfaces this limit lays close to $\sim 8\%$ ML (LT) and $\sim 11\%$ ML (RT), respectively. In addition, the barrier for the 2nd O_2 dissociation channel is lower on high-reduced $\text{TiO}_2(110)$ crystals than on low- and medium-reduced ones. Likewise the line shape of the O_2 -TPD-spectra depends on the crystal reduction state, and the O_2 desorption peak integrals show a highly non-linear dependence of the crystal reduction state. The presented results can be best explained within an ionosorption model: The adsorbates, O_2 molecules and O_{ot} adatoms, respectively, withdraw the Ti^{3+} excess charge from the near-surface region at $< 360\text{ K}$, and at temperatures $\geq \sim 360\text{ K}$ the oxygen species react with out-diffusing Ti interstitials.

2. Experimental

The STM and TPD experiments were performed in a UHV chamber with a base pressure in the low 10^{-11} Torr range equipped with a homebuilt, variable-temperature Aarhus STM, a quadrupole mass spectrometer (QMS), and standard facilities for sample preparation and characterization [60,61]. The Aarhus STM is capable of fast scanning and high resolution in a temperature range between 100 and 400 K [60]. Electrochemically etched tungsten tips were used for all STM measurements. The STM images presented in this study were acquired in constant current mode with a tunneling voltage of $\sim 1.25\text{ V}$ and a tunneling current of $\sim 0.1\text{ nA}$. Lower tunneling voltages and currents were also tested, and the results were found to be invariant in the covered parameter intervals. For the extraction of coverage based on the STM measurements at least total areas of $1300\text{--}2000\text{ nm}^2$ were scanned and analyzed. From previous studies we know that the analysis of STM images covering $\sim 1000\text{ nm}^2$ are sufficient in order to guarantee that the observed densities are representative for the whole sample surface [30,42,62].

The differentially pumped QMS was connected to the main chamber via a closed cone with a small aperture ($d \sim 3\text{ mm}$). To ensure that only molecules desorbing from the sample could reach the QMS, the cone was placed facing the sample at a distance of $\sim 1\text{ mm}$. The temperature of the sample could be varied from 100 K by cooling with liquid nitrogen to 1100 K by heating the back side of the sample radiatively and by electron bombardment. The sample temperature was measured using a K-type thermocouple spot-welded to the sample plate such that the thermocouple is in direct contact with the crystal face. The sample temperature was controlled and recorded by a Eurotherm temperature controller that contains an automatic compensation of ambient temperature changes. A calibrated pyrometer was used to double check the temperature of the samples during vacuum-annealing.

The PES experiments were carried out in an UHV end-station at the SX700 plane grating monochromator beam line at the ASTRID synchrotron radiation facility at Aarhus University [63]. The base pressure in this UHV chamber was likewise in the 10^{-11} Torr range. The PES data were acquired using a VG CLAM II spectrometer working at 30 eV pass energy. Valence band spectra were acquired with a photon energy of 47.5 eV, corresponding to the Ti 3p–3d resonance in order to maximize the intensity of the Ti 3d defect state in the band gap [26,64]. All PES spectra were acquired in normal emission geometry and normalized to the incident photon-flux. Spectra are plotted versus binding energy (BE) with respect to the Fermi level, E_{F} .

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