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Dissociation of formic acid on anatase TiO_2(1 0 1) probed by vibrational spectroscopy

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ABSTRACT

The interaction of formic acid with anatase TiO_2 (1 0 1) has been monitored by infrared reflection absorption spectroscopy (IRRAS) using a novel ultrahigh vacuum (UHV) system. It was found that HCOOH molecules do not adsorb intact on TiO_2 (1 0 1), as proposed previously, but dissociate yielding different formate species. The IR-bands observed in the IRRAS-data indicate the presence of a mono- and a bidentate species. It is proposed that the formation of the bidentate form requires the presence of oxygen vacancies.

1. Introduction

Titanium dioxide (TiO_2) attracts great interest from both fundamental and technological perspectives because of already existing applications of this material in the fields of solar energy conversion, water splitting, environmental treatments, etc. [1–4]. TiO_2 exists in different modifications, the two most important being rutile and anatase. It is known that most TiO_2 nanoparticles show the anatase form, which exhibits generally a substantially higher photocatalytic activity than that of rutile [4–6]. While the chemical processes occurring on the surface of rutile samples have been studied quite extensively, much less is known for anatase. In general, because of technical difficulties [7,8], experimental studies on well-defined single crystal surfaces are rather difficult for both, rutile and anatase.

Investigations of anatase nanoparticles (NPs) reveal that the (1 0 1)-orientation shows the largest contribution to the total surface area of the NPs, consistent with the fact that the (1 0 1) surface of anatase, a-TiO_2 (1 0 1), is the surface with the lowest free energy for this titania modification [9,10]. This surface is terminated by undercoordinated two-fold oxygen (O_{2c}) anions and five-fold Ti (Ti_{5c}) cations (see Fig. 1) [11]. Despite the high photocatalytic activity of anatase [6], it has been proposed that a-TiO_2 (1 0 1) is relatively inert. It has been reported in previous works that molecules like water, methanol and formic acid adsorb associatively on this surface [9,12–14]. It should be noted, however, that the reliable identification of many adsorbate species on anatase surfaces, even for the case of well-defined, macroscopic single crystal substrates, represents a major challenge. The reason for this difficulty in determining the nature of species formed after adsorption of molecular species results from the fact that vibrational spectroscopy, probably the most efficient method to identify chemical species, cannot be applied to surfaces of metal oxide single crystals in a straightforward fashion [7,8]. As a result of these technical problems, to our knowledge so far only one report describing vibrational spectroscopic studies on anatase single-crystal surfaces has been published [6].

In this paper, the interaction of formic acid with a-TiO_2 (1 0 1) surfaces has been monitored by IRRAS using a novel ultrahigh-vacuum (UHV) FTIRS apparatus [15]. Carboxylate groups are frequently used to anchor photosensitizers and other functional molecules to TiO_2 substrates [16,17]. As a result the binding of HCOOH, the simplest carboxylic acid, to anatase substrates is an important model system with regard to understanding the grafting of more complex molecules via carboxylate groups with this important oxidic substrate. The high-quality IR data presented here provide unambiguous evidence for the dissociative adsorption of HCOOH on a-TiO_2 (1 0 1), yielding a monodentate formate bound to

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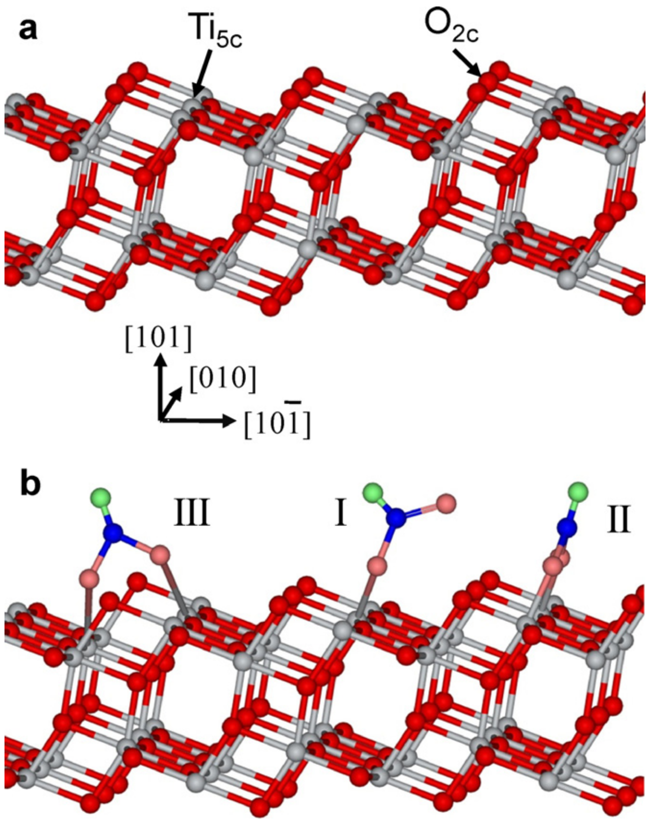

Fig. 1. (a) Ball-and-stick model of the anatase a-TiO_2 (1 0 1) surface in perspective view. (b) Schematic models of different formate species on a-TiO_2 (1 0 1). Red or pink ball: O; grey ball: Ti; blue ball: C; green ball: H. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

regular Ti_{5c}^{4+} sites of the perfect surface and an additional bidentate formate located at defect sites as represented in Fig. 1b.

2. Experimental

The infrared reflection absorption spectroscopy (IRRAS) measurements were carried out in a novel ultrahigh (UHV) apparatus which combines a state-of-the-art vacuum FTIR spectrometer (Bruker, VERTEX 80v) with a novel UHV system (PREVAC) as described in Ref. [15]. Briefly, its innovative design allows recording both IRRAS measurements at grazing incidence on perfectly flat substrates with a detection limit of $\Delta R/R = \sim 1 \times 10^{-5}$ and FTIR transmission measurements for polycrystalline powder samples [6,18–23]. Furthermore, this apparatus permits to record high-quality IR data with high sensitivity and long-term stability. These are essential prerequisites for monitoring the adsorption and subsequent transformation (e.g. induced by photons [6,19]) of molecular species adsorbed on oxide single-crystal surfaces. The base pressure of the measurement chamber is better than 1×10^{-10} mbar. The sample temperature can be varied between 100 K (cooling by flowing liquid nitrogen) and 1000 K (direct heating by electron impact).

The a-TiO_2 (1 0 1) single crystal used in this work was prepared by cutting and polishing a natural anatase mineral sample (MaTeck) with a very low impurity concentration of less than 100 ppm (0.01%). The single crystalline a-TiO_2 (1 0 1) surface with a size of $8 \times 5\,mm^2$ was cleaned by a standard procedure including cycles of Ar^+ ion sputtering (2.5 keV, 10 mA, 300 K, $p(Ar) = 5 \times 10^{-5}$ mbar) and annealing to 850 K. Previous work [24] has shown that this procedure yields atomically flat a-TiO_2 (1 0 1) surfaces with low defect concentrations. The defect density was checked independently by using CO as a probe molecule. CO adsorbed close to defects shows a shift of $\sim$10 cm^{-1}, thus allowing to determine the defect density directly [6,25]. The measurements were performed using IRRAS with a resolution of 4 cm^{-1} at a fixed grazing incidence angle of 80° along the [1 0 $\bar{1}$] azimuth. Formic acid was purified by applying several freeze-pump-thaw cycles before backfilling the measurement chamber through a leak valve. HCOOH exposures are given in units of Langmuir (L) ($1L = 1.33 \times 10^{-6}$ mbar s).

3. Results and discussion

Fig. 2a shows IRRAS data recorded after exposing the clean a-TiO_2 (1 0 1) surface to various amounts of HCOOH at room temperature. In the C–O stretching region four main IR bands can be resolved at 1646, 1598, 1386 and 1315 cm^{-1}. An additional weak band appears at 1362 cm^{-1}. All bands are positive, an important observation for IR-spectra recorded at an oxide surface (see discussion below). The relative intensities of these bands are found to change when HCOOH adsorption was carried out on a reduced a-TiO_2 (1 0 1) substrate as obtained by annealing in UHV to 950 K (see Fig. 2b). These vibrational bands are characteristic for formate species, revealing directly the dissociative adsorption of formic acid on a-TiO_2 (1 0 1) surfaces. The assignment of the observed IR bands to formate species is further supported by the heating experiments shown in Fig. 2b. After annealing the HCOOH-saturated a-TiO_2 (1 0 1) surface up to 500 K, all the IR bands remain nearly unchanged in position and intensity, which is in line with the thermal stability results of formate species reported on anatase powder samples [26]. Although also the binding energy of a hypothetical protonated formic acid adsorbate would be–according to theroricatl calculations – rather sizeable (0.92 eV [13]), the presence of such a species can be ruled out since the protonated acid would not show any C–O stretch modes in the frequency regime of 1300–1400 cm^{-1}.

The dissociative adsorption of formic acid is consistent with the acid-base character of Ti_{5c}–O_{2c} pairs on TiO_2 (1 0 1). The formate species produced by deprotonation of HCOOH must coordinate to the surface Ti_{5c} cations that act as Lewis acids, while the resulting H will bind to surface O_{2c} anions yielding hydroxyl groups. Unfortunately, no OH-related bands could be detected in the IR spectra recorded after exposure of the surface to formic acid. We explain the failure to observe such an OH stretch mode by the extremely small dynamic dipole moment of this species [27,28]. Similar problems have been reported in connection with IR spectroscopy carried out for formate species adsorbed on other metal oxide surfaces [29].

In principle, there are two possible adsorption configurations for formate species on an a-TiO_2 (1 0 1) surface, mono- and bidentate. They can be distinguished on the basis of the magnitude of the frequency splitting between the C–O stretching modes. The bands at 1647 and 1315 cm^{-1} observed in our experiments are separated by 332 cm^{-1} and are therefore assigned to the $\nu(C{=}O)$ and $\nu(C{-}O)$ modes of a monodentate formate. The second pair of IR bands at 1598 and 1362 cm^{-1} is separated by 236 cm^{-1}, typical for a bidentate formate species [29] and are attributed to the asymmetric $\nu_{as}(OCO)$ and symmetric $\nu_s(OCO)$ stretching vibrations, respectively. The band at 1386 cm^{-1} is assigned to the C–H bending mode $\delta(CH)$, which is proposed to be the same for both types of formate species.

According to the above analysis, the monodentate formate species is bound to surface Ti_{5c}^{4+} sites via one O atom as shown in Fig. 1b (type I). For bidentate formates the situation is more complicated, and it is necessary to first consider the principles of IRRAS at dielectric surfaces in more detail. For metal surfaces, the excitation of adsorbate vibrations by s-polarized IR light, the component of the E-vector of the incident light orientated parallel to the substrate, is negligible as a result of the dipole selection rule. For oxide

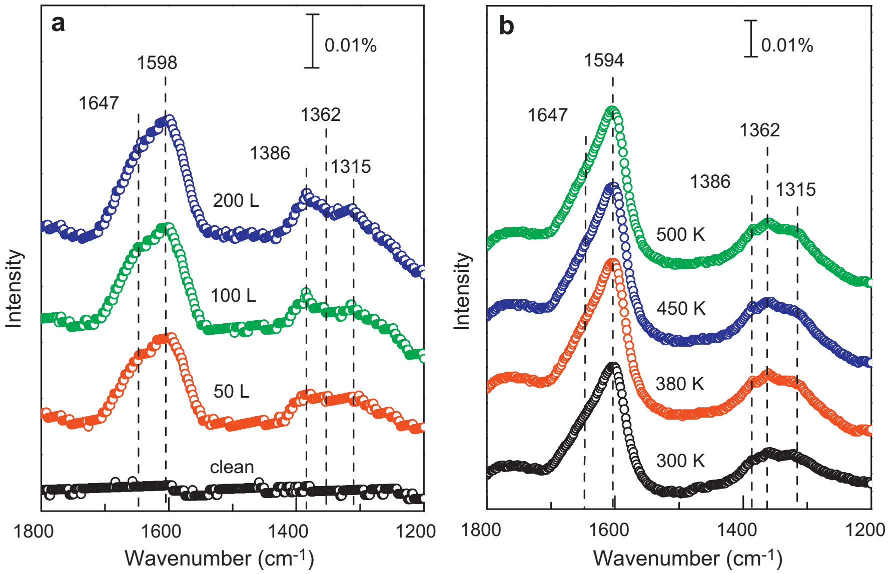

Fig. 2. (a) IRRAS data for HCOOH adsorbed on anatase TiO_2 (1 0 1) surfaces at room temperature as a function of dosage. (b) IRRAS data for 100 L of HCOOH adsorbed on the reduced anatase TiO_2 (1 0 1) surface prepared by over-annealing to 950 K. After exposure at 300 K, the sample was heated to the indicated temperatures. All spectra were recorded at 300 K with a resolution of 4 cm^{-1} in reflection at grazing incidence $\theta = 80°$.

(semiconductor or insulator) substrates, in contrast, both s- and p-polarized components of the incident E-vector couple to adsorbate vibrations. The reflectivity of dielectric surfaces can be calculated based on a classical three-phase model [30]. The occurrence of s-polarized vibrational bands always increase the reflectivity (i.e. vibrations give rise to negative bands in IR absorption spectra), while p-polarized bands are either positive or negative, depending on the incidence angle of the IR light and the optical properties of the substrate [21].

A possible adsorption geometry for the bidentate formate on a-TiO_2 (1 0 1) would be one where the two O-atoms coordinate to surface Ti_{5c} cations (type II in Fig. 1b), as observed on rutile r-TiO_2 (1 1 0) surfaces [29]. In this case the transition dipole moment of the $\nu_{as}(OCO)$ mode would be oriented parallel to the substrate, along the [0 1 0] azimuth (see Fig. 1b). Since the IR light is incident along the [1 0 $\bar{1}$] azimuth, the E-vector of the s-polarized component is orientated parallel to the [0 1 0] azimuth, and a strong coupling to the $\nu_{as}(OCO)$ mode of the (hypothetical) type II bidentate formate species should be present. This should result in a strong, negative IR band in the experimental data, as in the case of formic acid adsorbed on the (1 1 0) surface of the rutile modification of titania, r-TiO_2 (1 1 0) [29]. Since in the experiment both $\nu_s(OCO)$ and $\nu_{as}(OCO)$ modes of the bidentate formate exhibit a positive sign, these vibrations must be excited predominantly by the p-polarized component of the incident IR light. An orientation like that labeled "type II" in Fig. 1b can thus be excluded on the basis of the present experimental data. Instead, we propose the adsorption geometry as shown in Fig. 1b (type III), where one O interacts with a regular Ti_{4c} cation, whereas the other O binds to a Ti_{5c} cation exposed within an O_{2c} vacancy. In this case, both $\nu_{as}(OCO)$ and $\nu_s(OCO)$ modes will exhibit transition dipole moments with large components orientated normal to the surface, which can couple effectively to p-polarized light. The conclusion on the correlation of the bidentate species with O-defects is further corroborated by additional IR experiments discussed below.

It should be noted that we cannot completely rule out the presence of a small amount of a chelating formate configuration formed at doubly unsaturated Ti sites. We can only conclude that in our experiments the intensities of the characteristic IR-bands of such a species were below the detection limit.

In Fig. 3 we compare the IRRAS data recorded after exposing differently pretreated a-TiO_2 (1 0 1) surfaces to HCOOH at room temperature. For the substrate pretreated by an over-annealing to 950 K (curve B), which will result in a relatively high density of O-vacancies, the intensity of the bidentate formate-related IR bands (1604 and 1362 cm^{-1}) is found to be substantially increased relative to those on a-TiO_2 (1 0 1) prepared by the standard procedure yielding a fairly low density of O-defects (curve A), suggesting a correlation of bidentate formate density with O-vacancy concentration. Interestingly, according to recent STM studies [24], the reduced anatase TiO_2 (1 0 1) contains predominantly O vacancies in the subsurface region, whereas the concentration of surface O vacancies is rather low. The observation that bidentate formates are bound to surface O_{2c} vacancy sites thus indicates the adsorbate-mediated diffusion of O vacancies to the surface. A similar effect has been reported for other oxide substrates [31,32].

In the second set of experiments we have decreased the number of available oxygen vacancies on the a-TiO_2 (1 1 0) substrate by exposing the reduced surface to molecular oxygen at 300 K prior to the adsorption of HCOOH. The corresponding data are shown in curve C of Fig. 3 and demonstrate that the bands at 1598 and 1362 cm^{-1} are attenuated significantly, whereas the monodenate formate-related band intensities are hardly affected. It has been proposed that O_2 adsorption on the reduced TiO_2 (1 0 1) surface occurs at sites close to subsurface O vacancies and is accompanied by the transfer of defect electrons to the molecular adsorbate, yielding peroxide (O_2^{2-}) and/or superoxide (O_2^{-}) species [33]. As a result, the vacancy-sites are blocked, thus explaining the attenuation of the bidentate formate bands. The results of these blocking experiments thus nicely corroborate the proposed adsorption geometry of the bidentate formate.

Finally, we also studied the interaction of formic acid with the a-TiO_2 (1 0 1) surface at low temperatures. After HCOOH adsorption at 120 K, the IRRAS data (not shown) exhibit the same absorption bands as observed at room temperature, revealing the formation of formate species via deprotonation of HCOOH already at this low temperature. This finding indicates that the activation energy for deprotonation must be fairly low.

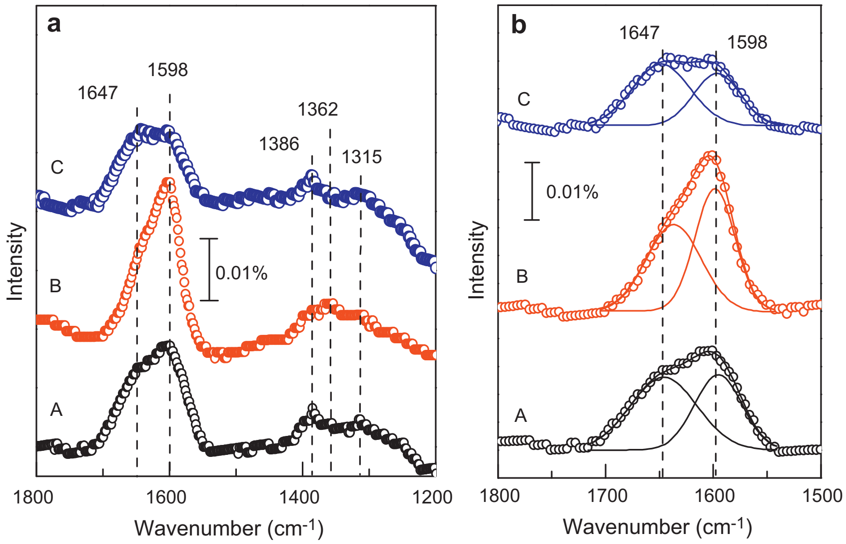

Fig. 3. (a) IRRAS data for HCOOH adsorbed on differently treated anatase TiO_2 (1 0 1) surfaces at room temperature: (A) annealed to 850 K; (B) over-annealed to 950 K; (C) first over-annealed to 950 K and then 100 L of O_2 pre-dosed at room temperature. (b) The solid line was obtained by fitting Gaussian functions to the experimental data. All spectra were recorded at 300 K with a resolution of 4 cm^{-1} in reflection at grazing incidence $\theta = 80^\circ$.

4. Conclusions

In summary, the present IRRAS data demonstrate that the room-temperature adsorption of formic acid on a-TiO_2 (1 0 1), the most important and energetically most stable face of anatase powder particles, results in deprotonation, yielding two different types of formate species. One is a monodentate formate with one O-atom coordinated to a regular surface $Ti_{5c}{}^{4+}$ cation. In addition, a bidentate formate is identified which is assigned to a species residing at surface O vacancy sites with one oxygen atom bound to a regular Ti_{4c} cation and the second to a defect Ti_{5c} cation. These findings demonstrate that the anatase TiO_2 surface chemistry of carboxylic acid is quite different from that of rutile surfaces and will allow for a better understanding of carboxylic-acid mediated grafting of larger molecules to anatase substrates, e.g. in the context of organic solar cells and photocatalysis [2,4].

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