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Co-adsorption of oxygen and formic acid on rutile TiO₂ (110) studied by infrared reflection-absorption spectroscopy

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KEYWORDS: TiO₂, infrared reflection absorption spectroscopy, formic acid, bicarbonate

Abstract

Adsorption of formic acid and co-adsorption with oxygen have been investigated on the rutile TiO₂(110) surface using p- and s-polarized infrared reflection-absorption spectroscopy (IRRAS) at O₂ exposures between 45 L to 8100 L. On the clean surface formic acid dissociates into a formate ion (formate) and a proton. Formate binds to two five-folded coordinated Ti atoms in the troughs along the [001] direction, and the proton binds to neighboring bridging O atoms. Exposure of adsorbed formate to O₂ leads to a decrease in the asymmetric $\nu_{\text{as}}(\text{OCO})$ band at

1532 cm^{-1} and to a concomitant formation of a new vibration band at 1516 cm^{-1} . From the s- and p-polarized IRRAS measurements performed at different O_2 exposures, surface pre-treatments and substrate temperatures, and by comparisons with previous reports, we conclude that the new species is a surface carbonate, which is formed by reaction between formate and oxygen adatoms on the surface. The σ_v reflection plane of the carbonate molecule is oriented along the [001] direction, i.e. the same direction as the adsorbed formate molecule. On the clean $\text{TiO}_2(110)$ surface exposed to O_2 prior to formic acid adsorption, similar results are obtained. The reaction rate to form carbonate is found to follow first-order kinetics, with an apparent activation energy of $E_r = 0.25 \text{ eV}$.

1. Introduction

Titanium dioxide (TiO_2) is an important material in renewable energy and environmental applications and has been the subject for numerous studies on photocatalytic air and water cleaning[1,2] photocatalytic solar fuel generation[3], sensors[4] and photovoltaics[5]. Common for all these applications is that surface processes determine the function of the material. Our understanding of the elementary surface reactions on TiO_2 surfaces have increased considerably during the past two decades but several important fundamental questions remain[2,6]. Most fundamental surface science studies have focused on the single crystal rutile $\text{TiO}_2(110)$ surface, as it is the thermodynamically most stable surface with the lowest surface energy, and large area samples can readily be obtained that are suitable for a wide range of experimental investigations. Consequently this surface has become the prototype surface for single crystal investigations of photo-induced molecular reactions and adsorbate-surface interactions on TiO_2 [6–8]. The $\text{TiO}_2(110)$ surface exposes alternating rows of bridging oxygen atoms, O_{br} , with a two-folded

coordination, along the [001] direction, and five-folded coordinated titanium, Ti_{5c} , atoms in the troughs in between.

In many photocatalytic processes formate is a key intermediate species, e.g. in oxidation of organic molecules and in photo-synthesis of alcohols and hydrocarbons from CO_2 and H_2 . Consequently, adsorption of formate on TiO_2 have been extensively studied experimentally and theoretically on nanocrystalline[9–14] and single crystal[15–24] TiO_2 . On the rutile $TiO_2(110)$ surface formate adsorption occurs by deprotonation of formic acid ($HCOOH$) into one H^+ and one formate ion $HCOO^-$ that binds to O_{br} , and Ti_{5c} atoms, respectively[15,16,19].

In photocatalytic processes on TiO_2 , O_2 acts as an electron acceptor and as an oxygen radical source. Thus the interaction between oxygen and the adsorbed molecule on the photocatalyst surface is of paramount importance in the rapidly growing field on photocatalysis. . The adsorption mechanisms for O_2 on the $TiO_2(110)$ surface have previously been studied both at cryogenic and elevated temperatures. In the temperature range between ~ 150 K and 400 K, O_2 is reported to either dissociate at O vacancies and bind to the O vacancy site, O_{vac} , and surrounding Ti_{5c} atoms[25,26], or dissociate at Ti_{5c} sites to form a pair of oxygen adatoms[27,28].

Vacuum based infrared reflection-absorption spectroscopy (IRRAS) – sometimes called infrared external reflection spectroscopy (IRES) – is a useful technique to study molecular adsorbates and chemical reactions on the surface of metal oxides. Not only can the chemical reactions on the surface be followed, it is also possible to get information about the orientation of the adsorbate on the surface by utilizing s- and p-polarization of the IR light. This method has previously been used to investigate the interaction between TiO_2 and water, gaseous species such as NO, CO and CO_2 , as well as carboxylic acids[15,16,29–34].

Here we report of the interaction between formate and oxygen on the rutile TiO_2 (110) surface as studied by IRRAS. Our results show that adsorbed formate interacts with O_2 to form a bicarbonate surface complexes that are oriented along the troughs in the [001] direction. The reaction is activated with an apparent activation energy of 0.25 eV. We propose a reaction scheme and determine the reaction rates for the elementary reaction steps.

2. Experimental

The experimental setup has been described in detail elsewhere[16,34]. In brief, IRRAS spectra, R_a/R_0 were recorded in a UHV chamber with a base pressure of $\sim 2 \times 10^{-10}$ mbar, using a FTIR spectrometer (Bruker IFS 66v/S, Ettlingen, Germany) and an external LN2 cooled narrow band MCT detector (Infrared Associates, CA, USA) coupled to the UHV chamber through KBr windows. Here R_a and R_0 denote the reflectivity with and without the adsorbate layer, respectively. The entire IR beam path outside the UHV chamber was evacuated to 2 mbar. A wire-grid polarizer (Specac, UK) mounted in the beam path was used to change the polarization of the incident IR light on the sample. Each spectrum was averaged over 2048 scans, corresponding to ≈ 7 min collection time, using a spectral resolution of 4 cm^{-1} . All presented spectra was acquired with p-polarized light incident along the [001] direction, unless otherwise stated.

A 20×20 mm rutile single crystal (Pi-Kem Ltd, Staffordshire, UK) was prepared by repeated Ar^+ sputtering and annealing cycles. A typical sample preparation cycle consisted of 10 min sputtering (1 keV, 1 μA ion current on the sample) followed by 10 min annealing at 900 K in 1×10^{-6} mbar of O_2 (Air Liquid, 99.998% purity) by backfilling the UHV chamber and subsequently 10 min annealing in UHV conditions. This procedure was repeated twice to re-

oxidize the surface before two additional sputter and annealing cycles at 900 K in UHV were performed. Low energy electron diffraction (LEED; OCI Vacuum Microengineering, BD800IR) was measured before IRRAS measurement to confirm the surface structure. The sample preparation was considered complete when a clear (1×1) pattern, typical for the TiO₂(110) surface, was observed. The LEED pattern was also used to align the azimuthal angle of the TiO₂(110) crystal so that the polarized IR light was incident in the [001] direction, along the bridging oxygen rows. Formic acid (HCOOH puriss, Fluka, Schnell-dorf, Germany) was dosed through a μm-sized pinhole aperture from a directed gas dosing setup, which was mounted on a translation stage and connected to a reservoir of liquid formic acid through a series of valves. Prior to dosing, the formic acid source was subjected to several freeze-thaw cycles. Formic acid dosing was performed for 60 s, after which the gas doser was directly pumped for 60 s. This dosing procedure results in saturation coverage of formate, i.e. $\theta_{\text{HCOO}} = 0.5$ [16]. Formic acid dosing was either done on the clean, as-prepared TiO₂(110) surface, or after the surface was exposed to different doses of O₂ (Air Liquid, 99.998% purity) between 45 L and 8100 L (1 L = 10⁻⁶ Torr s), as obtained by backfilling the UHV chamber. Control experiments using water vapour was performed using the same directed gas dosing setup by exchanging the formic acid reservoir to de-ionised water, and employing the same pump-freeze-thaw procedure.

3. Results

3.1 Formic acid adsorption

Formic acid deprotonates and binds in a bidentate configuration to two Ti_{5c} atoms in the troughs along the [001] [15,16,19]. Using p-polarized IR-light this gives rise to the well-known IRRAS spectrum shown in Figure 1, where the asymmetric and symmetric $\nu(\text{OCO})$ bands are

located at 1532 cm^{-1} and 1360 cm^{-1} , respectively. The bands at 1373 cm^{-1} and 1388 cm^{-1} are due to the $\delta(\text{C-H})$ modes which couple to the normal and parallel component of the incident IR light, respectively[16].

3.2 Co-adsorption of formic acid and oxygen

Exposure of a TiO_2 (110) pre-covered with a saturation coverage of formate to O_2 results in formation of a new vibrational band at 1516 cm^{-1} in the IRRAS spectra. At a pressure of $P_{\text{O}_2} = 1 \times 10^{-6}$ mbar this new peak is clearly visible as a shoulder on the low energy side of the $\nu_{\text{as}}(\text{OCO})$ peak after 30 min of exposure, and after 90 min it becomes the dominant peak (Figure 2a). At lower partial pressure, $P_{\text{O}_2} = 5 \times 10^{-7}$ mbar, this process takes longer time (Figure 2b), and at even lower pressure, $P_{\text{O}_2} = 1 \times 10^{-7}$ mbar, no signs of this new band can be seen even after 3 h of exposure (Figure 2c). Once the new peak is formed, the IRRAS spectra cannot be reversed to the original formate spectra (as shown in Figure 1) by evacuating the oxygen from the UHV chamber. Thus O_2 induces an irreversible reaction that converts the bidentate bridge bonded HCOO to a new species. The same spectral changes take place when the order of exposure is reversed, i.e. the clean $\text{TiO}_2(110)$ surface is first exposed to O_2 and thereafter HCOOH when the O_2 doses are larger than 100 L (Figure 3). The intensity of the new 1516 cm^{-1} band grows exponentially with the O_2 exposure. The new species, characterized by the 1516 cm^{-1} band, which is formed upon reaction with formate and O_2 is thermally stable. This is evidenced by the fact that no additional changes in peak positions occur during 3 h in UHV conditions (Figure 4), as well as the temperature dependent measurements presented below (Section 3.4). A small red-shift, $\sim 2\text{ cm}^{-1}$, of the $\delta(\text{C-H})$ band is seen in conjunction with the formation of the new absorption band at 1516 cm^{-1} , whereas the position of the symmetric $\nu_{\text{s}}(\text{OCO})$ band remains at

the same position, 1360 cm^{-1} , irrespectively of the O_2 exposure and formation of the new absorption band at 1516 cm^{-1} .

3.3 Formate and water

To investigate the possibility whether residual water in the UHV chamber contributes to the spectral changes, additional measurements with controlled water exposure were made both before and after formic acid exposure. It is known that even small amounts of water in the UHV chamber can induce reactions with the $\text{TiO}_2(110)$ surface, and dissociate at O vacancy sites[35]. Exposing the $\text{TiO}_2(110)$ surface to water, employing an equivalent dose as was used to obtain saturation coverage of formate, followed by formic acid dosing yield IRRAS spectra identical to those that are obtained when formic acid is dosed directly on the pristine $\text{TiO}_2(110)$ surface, i.e. spectra identical to that reported in Figure 1. This is in agreement with earlier reports that water does not stick on the $\text{TiO}_2(110)$ surface at 300 K[33,36–38]. The same results were also obtained when water was dosed on a surface saturated with formic acid. Similarly, no changes in the spectra are seen when a formate covered surface is kept for 3 h in UHV exposed to background water adsorption (Figure 5). In the latter case, a small decrease of the formate band is seen and will be analysed in more detail in Section 4.

3.4 Temperature dependence of formic acid and oxygen interaction

With increasing substrate temperature the intensity of the 1516 cm^{-1} shoulder increases both when a pristine $\text{TiO}_2(110)$ surface is exposed to $> 100\text{ L O}_2$ (Figure 6), and when a formate saturated surface is exposed to O_2 (Figure 7). Higher temperatures give a more pronounced band at 1516 cm^{-1} , and simultaneously a decrease in the formate band at 1532 cm^{-1} . At 343 K the peak

at 1532 cm^{-1} has almost disappeared, whereas at lower temperatures it is clearly seen as a shoulder on the large peak at 1516 cm^{-1} . Peak deconvolution shows that the 1532 cm^{-1} peak decreases exponentially, and that the 1516 cm^{-1} peak increases exponentially with time (Figure 8). At the highest temperature, 343 K, the formate coverage is slightly less than at lower temperatures, as is evident from Figure 6 and 8. This can be attributed to removal of formate by either desorption of loosely bonded formate or by dehydrogenation reaction[39], which does not depend on whether O_2 is supplied before (not shown) or after (as in Figure 7) formic acid dosing.

4. Discussion

4.1 O_2 interaction with adsorbed formate

It is well-known that formic acid dissociates as it adsorbs on the TiO_2 (110) surface, viz. $\text{HCOOH} \rightarrow \text{HCOO}_{\text{ad}} + \text{H}_{\text{ad}}$. The proton binds to bridging oxygen, O_{br} , to form a bridging hydroxyl OH_{br} species. On the non-defective surface, the formate ion forms a bidentate species orientated parallel to the bridging oxygen rows in the [001] direction, with the two O atoms bonded to two $\text{Ti}_{5\text{c}}$ atoms[15,16,19,20,22,39–42]. This species has also been denoted type A in the literature[15,16]. Different minority formate species bonded in different configurations have also been reported. These minority species include a formate molecule oriented perpendicular to the oxygen bridging rows with one O atom bonded to a $\text{Ti}_{5\text{c}}$ atom and the other O atom bonded to a O_{vac} site (type B)[24,43]. Formate bonded to a $\text{Ti}_{5\text{c}}$ atom and a hydroxylated O_{vac} (type D) has also been reported[16,44]. Finally, a formate species aligned in the [001] direction and adsorbed on the O_{br} row, with one O atom bonded to a bridging O_{vac} site and hydrogen bonded to a O_{br} (HO_{br}) atom, has been observed by STM (type C)[24]. On the perfect surface, saturation coverage of type A formate corresponds to a coverage of $\theta_{\text{A, sat}} = 0.5$, calculated as the ratio to

the number of Ti_{5c} sites, corresponding to a 2×1 configuration of formate. The O_{vac} concentration, which depends on surface pre-treatment, is typically of the order $\theta_{\text{Ovac}} \sim 0.06$ [7,33,35], and may vary ± 0.04 depending on the detailed surface preparation procedure. Thus, the amount of minority species on the surface will vary accordingly. On a reduced surface, a maximum coverage of bridging O_{vac} has been reported to be $\theta_{\text{Ovac}} = 0.1$ [35,45]. As we discuss below, residual water adsorption is expected to decrease the O_{vac} concentration – even under UHV conditions.

From Figure 9 it is evident that p-polarized IR-light, incident in the $[001]$ direction, couples to the symmetric $\nu_s(\text{OCO})$ and the asymmetric $\nu_{\text{as}}(\text{OCO})$ vibrations in type A and C species and to the normal component of the $\nu_s(\text{OCO})$ and $\nu_{\text{as}}(\text{OCO})$ vibrations in type B and D species[16]. In contrast, s-polarized light incident in the $[001]$ direction couples only to the $\nu_{s,\text{as}}(\text{OCO})$ modes in type B and D species, and not to type A and C species. Based on these observations, we can experimentally exclude the possibility that the changes seen in Figure 2 are due to conversion from type B and/or D species (which can be observed with s-polarized light incident in the $[001]$ direction) to species C (which can only be observed with p-polarized light incident in the $[001]$ direction, and not s-polarized light) for two reasons. First, we have previously shown by DFT calculations, that the asymmetric $\nu_{\text{as}}(\text{OCO})$ vibration frequency for species C is upshifted more than 100 cm^{-1} compared to species A. In contrast, a downshift of the vibrational frequency is here observed[16]. Second, by employing s-polarized light, incident in the $[001]$ direction, the appearance of either type B and D species, if present, would be observed in the IRRAS spectra as well as their decreasing signal due to conversion into the new species found at 1516 cm^{-1} with p-polarized light. This is not observed in the IRRAS measurements utilizing s-polarized light, Figure 10; employing an O_2 pressure $P_{\text{O}_2} = 1 \times 10^{-6} \text{ mbar}$ no peaks at all is seen in the IRRAS

spectra. Even though the reflectance ($\Delta R/R_0$) is slightly lower for s-polarized light compared to p-polarized light at the angle of incidence employed here[16], the magnitude of the changes seen for p-polarized light in Figure 2a would be large enough to be observed with s-polarized light.

As shown in Figures 2-4, 6 and 7, the same O₂-induced chemical reactions of formate occur regardless whether O₂ is exposed before or after adsorption of formic acid, provided that the O₂ dose/pressure is sufficiently large. The only difference in the spectra is the rate of the reaction, i.e. how much formate that is reacted. Supplying oxygen after formic acid adsorption results in a gradual change with time. We can exclude that these differences are due to activated reactions of formate with O_{vac} sites by the following arguments. First, O₂ has been reported to dissociate on TiO₂ (110) surfaces containing O_{vac} and OH_{br} species and thereby healing the O_{vac} sites and form O_{ad} atoms, bonded to Ti_{5c} sites, on the TiO₂ (110) surface[46,47]. Thus if O_{vac} is present on the surface, as a result of the sample preparation procedure, it will be healed by the O₂ dosing made prior to the formic acid exposure. As there are no differences in the appearance of the new species at 1516 cm⁻¹ regardless whether oxygen is supplied post or prior to formic acid dosing, it proves that reaction with O_{vac} is not the cause of the formation of the new species. Besides, without oxygen exposure, no changes are seen in the IRRAS spectra, except slow removal of formate associated with the 1532 cm⁻¹ band, about 0.04 ML per hour. Thus, reaction of formate with O_{vac}, does not explain the O₂-induced changes in the IRRAS spectra. Furthermore, as a remark, O_{vac} sites that are known to be formed employing our sample preparation procedure[7,8] rapidly react with water present in the gas-phase in the vacuum chamber. Even at UHV pressures in the 10⁻¹⁰ mbar range O_{vac} sites have been reported to be hydroxylated with water within a couple of minutes, thus forming HO_{br} species, viz. $\text{H}_2\text{O}_g + \text{O}_{vac} \rightarrow 2\text{OH}_{br}$ [8,35,48]. Hence, most of the O_{vac} which are formed after preparation of the crystal in our experiments can be

assumed to be healed and hydroxylated prior to the O₂ exposure experiments[16], and thus the O_{vac} concentration is most likely very small.

In previous studies several different species have been reported to form upon reaction with formic acid on the rutile TiO₂ surface. TPD measurements have shown the presence of small amounts of formaldehyde at elevated temperatures around 550 K. From ¹⁸O isotope experiments it was shown that two formate molecules reacts in a secondary pathway at O_{vac} sites to form formaldehyde and carbon dioxide[19,36,49]. DFT calculations of carboxylic acids on rutile TiO₂ (110) surface have shown that the difference in binding energy between formate surrounded by a free hydrogen atom, and acetic acid, hydrogen carbonate or carbonate surrounded by a free or two free hydrogen atoms, is very small[50]. However, our collected IRRAS results show that the new species cannot be due to formaldehyde or acetic acid surface complexes as can be seen by the following analysis of our data. Figure 8 shows that the coverage of the new species increases simultaneously as the formate coverage decreases and that the total coverage on the surface is constant, assuming that the IR cross section is the same for the 1532 cm⁻¹ and 1516 cm⁻¹ bands, which is reasonable since they both must be of C-O origin because these are the only possible species that can form from HCOOH and O₂. As we are only supplying oxygen, carbon mass balance requires that the carbon atom in the formate molecule is transformed into other surface species in a 1:1 stoichiometric reaction in order to maintain the total coverage. Conversely, if no oxygen is supplied formate is not reacted to the new species. These results exclude the possibility that two surface formate molecules react to yield one formaldehyde molecule and CO₂. Nor will acetic acid formation maintain the 1:1 balance of the $\nu_{as}(\text{C-O})$ mode. Moreover, it is well-known the formaldehyde $\nu(\text{C=O})$ bands of isolated molecules occur at much higher frequency (> 1600 cm⁻¹) on TiO₂ [11,51], and is unlikely that any aldehyde surface complex will produce carbonyl

bands as low as 1516 cm^{-1} . Similarly no $\nu(\text{C-C})$ or $\nu(\text{C-H})$ vibrational band that can be associated with acetic acid are observed in the IRRAS spectra.

From the results in Figure 5 we can also rule out that the 1516 cm^{-1} peak is due to reactions with water from the gas-phase. Figure 11 shows the results of long-time exposure (up to 24 hours) of the formate saturated $\text{TiO}_2(110)$ surface to the background UHV chamber gas. No vibrational band at 1516 cm^{-1} is seen in those experiments. Instead a significant upshift ($\sim 15\text{ cm}^{-1}$) of the $\nu_{\text{as}}(\text{OCO})$ peak to 1546 cm^{-1} is observed simultaneously as the formate $\nu_{\text{as}}(\text{OCO})$ peak at 1532 cm^{-1} decreases. The decreased intensity of the 1532 cm^{-1} peak can be explained by removal of loosely bonded formate from the surface into the gas phase by dehydrogenation reaction. Dehydrogenation of formate has been reported to occur at temperatures below 450 K on surfaces with large coverage of formate[39,52]. The thermal induced removal rate of formate was determined at different temperatures (see Section 4.2 below), and agrees quantitatively with the decrease in peak area seen in Figure 11. The appearance of the 1546 cm^{-1} band can be explained by formation of formate ions on the surface due to adsorption of H_2O and CO_2 that are released from the liquid nitrogen cooled sample holder during the overnight experiments when the cooling of the sample holder was not maintained. Furthermore, formic acid that is condensed on the cooled surfaces is also released and contributes to appearance of formate ions in these latter experiments. These formate ions will be hydrogen bonded to the rutile surface. A hydrogen-type bonding of formate will cause an up-shift of the frequency, and this has previously been observed for formic acid exposure on TiO_2 powders and films in atmospheric conditions where aqueous formic acid ions exhibit an upshift to $\sim 1590\text{ cm}^{-1}$ [10,13].

In contrast, formation of hydrogen carbonate or carbonate (HCO_3 or CO_3) surface complexes maintain carbon mass balance, and only requires the interaction with an oxygen adatom, O_{ad} , or

hydroxyl group on the surface. TPD measurements have shown that O₂ does not adsorb on the defect-free TiO₂ (110) surface in the pressure ranges and temperatures used in these experiments; only at cryogenic temperatures O₂ adsorption occurs[53]. However, as mentioned above, O₂ adsorption and dissociation can occur if O_{vac} or OH_{br} species are present on the surface. The O₂ adsorption energy is reported to increase from 0.2 eV to 2 eV with increasing OH coverage[26,54,55]. The exact mechanism for the creation of O_{ad} atom on the surface have been reported to be different depending on the magnitude of the oxygen dose[8,46,56,57]. These O_{ad} species have previously been reported to be reactive and stable. STM images have shown O_{ad} atoms present on the TiO₂ (110) surface at 300 K, and TPD data suggest that they exist on the surface at temperatures up to 600 K[25,58]. If water is present, even in very small amounts, in the UHV chamber, O_{ad} can react with water and form an OH group bonded to a Ti_{5c} atom in the troughs, OH_t. As discussed above, the surface preparation procedure employed here results in small amounts of OH_{br} on the surface (but no, or little, O_{vac}). Thus under our experimental conditions we expect that O₂ exposures lead to dissociative adsorption of O₂ and formation of both O_{ad} and OH_t species on the surface, even at the highest sample temperatures employed in our experiments (343 K), as recombination of OH_t species into water occurs above 400 K[56]. In our case we thus conclude that condition for formation of carbonate surface complex is realized since exposure of a pristine surface to formic acid only yields formate, and does not display a vibrational band at 1516 cm⁻¹.

IR spectroscopy measurements of bicarbonate on a mixture of rutile and anatase TiO₂ powder have shown that the asymmetric ν_{as}(CO) vibrational frequency occurs at about 1560 cm⁻¹ [59], i.e. higher than the frequency for the new band at 1516 cm⁻¹ observed here. It is therefore likely that the 1516 cm⁻¹ band can be associated with the ν_{as}(CO) mode of a surface carbonate HCO₃

species, $\text{O}\cdots\text{O}-\text{COH}$, which is a precursor to bicarbonate. In conclusion, our collected data presented in Figures 2 – 7, and available literature, strongly support that surface carbonate species, $\text{O}\cdots\text{O}-\text{COH}$ (HCO_3, ads), are formed by reactions with formate and O_{ad} , or with surface OH that is formed by reactions of O_{ad} and protons from formic acid dissociation or dissociated residual gas H_2O .

4.2 Reaction kinetics

The kinetics of the formate reaction as a function of O_2 exposure on a surface saturated with formate was analyzed by deconvolution of the $\nu_{\text{as}}(\text{OCO})$ bands IRRAS spectra in the 1450 to 1600 cm^{-1} region to quantify the 1532 cm^{-1} and 1516 cm^{-1} bands. From the discussion in the preceding paragraphs we assume that type A formate is oxidized to a hydrogen carbonate surface complex according to following reaction:

which is governed by first-order reaction kinetics, viz

$$\frac{d\theta_A}{dt} = -(k_t + k_r)\theta_A, \quad (1)$$

$$\frac{d\theta_X}{dt} = k_r\theta_A, \quad (2)$$

where θ_A is the coverage of type A formate, θ_X is coverage of surface bicarbonate HCO_3 associated with the 1516 cm^{-1} band, k_r is the reaction rate, and k_t is the thermal removal rate of formate from the surface into gaseous species by dehydrogenation reaction (or possibly by

desorption of loosely bonded formate). Solving for θ_A and θ_X , with the initial condition ($t = 0$) that the surface is saturated, i.e.

$$\theta_{A,0} + \theta_{X,0} = 0.5, \quad (3)$$

yields:

$$\theta_A(t) = \theta_{A,0} e^{-(k_r+k_t)t} \quad (4)$$

$$\theta_X(t) = \frac{\theta_{A,0}k_r}{(k_r+k_t)} (1 - e^{-(k_r+k_t)t}) + \theta_{X,0}. \quad (5)$$

The concentrations of A and X were determined by the measured IRRAS absorbance A_A and A_X , viz.

$$A_A(t) = A_{A,0} e^{-(k_r+k_t)t}, \quad (6)$$

$$A_X(t) = \frac{A_{A,0}k_r}{(k_r+k_t)} (1 - e^{-(k_r+k_t)t}) + A_{X,0} \quad (7)$$

where $A_{A,0}$ and $A_{X,0}$ is the initial absorbance at $t = 0$. k_r and k_t was determined from eqn. 6 and 7 at T = 273 K, 303 K, 323 K and 343 K, and is shown in Table 1. The formate (θ_A) and $\text{HCO}_{3,\text{ads}}$ coverages (θ_X) were determined by converting the $A_A(t)$ and $A_X(t)$ data to coverage by assuming that the sum of $A_{A,0}$ and $A_{X,0}$ corresponds to saturation coverage according to Eqn. 3. The IR cross sections for excitation of the HCOO_{ads} and $\text{HCO}_{3,\text{ads}}$ $\nu(\text{C-O})$ mode are here assumed to be the same, and absorbance data for the two species can directly be translated into coverage. The

first 150 minutes of O₂ exposure are used to determine the rate constants, since at longer times the reaction is completed at high temperatures and high O₂ pressures. The determined rate constants show, as expected, that with increasing temperature the conversion rate increases. An increase by a factor of ~10 is seen when the temperature is raised from 273 K to 343 K. k_t was also determined separately at 273 K without O₂ exposure and was determined to be $0.7 \times 10^{-3} \text{ min}^{-1}$, which agree well with the value derived from the kinetic analysis.

Arrhenius analysis of the temperature dependence of the reaction rates of formate to HCO_{3,ads}, $k_r = k_r(T)$, and dehydration, $k_t(T)$, viz.

$$k_{r,t} = k_0 e^{-\frac{E_{r,t}}{k_B T}} \quad (7)$$

where $E_{r,t}$ is the activation energy for the reaction to HCO_{3,ads} and dehydration, respectively, k_B is Boltzmanns constant, yield a linear dependence of k_r and k_t as a function of $1/T$ (Figure 12). The activation energy for reaction into HCO_{3,ads} is estimated to be $E_r = 0.25 \text{ eV}$, and the activation energy for the dehydration reaction is $E_t = 0.19 \text{ eV}$. A similar activation energy, 0.16 eV, for the dehydrogenation of formate into CO₂ and H₂ have previously been reported by Onishi and co-workers[39].

Conclusions

Using polarized IRRAS the interaction between formic acid, adsorbed on the rutile TiO₂ (110 surface), and O₂ have been studied. The IRRAS measurements show that upon exposure to O₂ adsorbed formate reacts with oxygen, as evidences by the disappearance of the band at 1532 cm^{-1} due the $\nu_{\text{as}}(\text{OCO})$ mode in formate, and the appearance of a new vibrational band at 1516 cm^{-1} .

No deprotonation occurs as the $\delta(\text{C-H})$ bands remains unchanged in position and intensity. It is concluded that oxygen adatoms, O_{ad} , or terminal OH_t are formed on the surface, as a result of the O_2 exposure, and these adatoms react with the formate to form surface carbonate species, $\text{HCO}_{3,\text{ad}}$. The polarized IRRAS measurements show that $\text{HCO}_{3,\text{ad}}$ are orientated along the [001] direction, similar as the formate molecules, i.e. O_{ad} attach to formate by reactions along the troughs to form $\text{O}\cdots\text{O-COH}$ surface complexes. Measurements made at different temperatures between 273 K and 343 K show that the reaction between formate and oxygen is thermally activated with activation energy of $E_{\text{r}} = 0.25$ eV. The activation energy for the removal of formate into gaseous species by dehydrogenation was estimated to be $E_{\text{rem}} = 0.19$ eV.

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Tables

Table 1. Reaction kinetics determined at different temperatures with an oxygen partial pressure of 1×10^{-6} mbar using a first order kinetics reaction.

Temperature	$k_r + k_t$	k_r	k_t
273 K	$0.3 \times 10^{-2} \text{ min}^{-1}$	$0.2 \times 10^{-2} \text{ min}^{-1}$	$0.9 \times 10^{-3} \text{ min}^{-1}$
303K	$0.5 \times 10^{-2} \text{ min}^{-1}$	$0.4 \times 10^{-2} \text{ min}^{-1}$	$1.0 \times 10^{-3} \text{ min}^{-1}$
323K	$1.2 \times 10^{-2} \text{ min}^{-1}$	$0.9 \times 10^{-2} \text{ min}^{-1}$	$3.2 \times 10^{-3} \text{ min}^{-1}$
343K	$2.3 \times 10^{-2} \text{ min}^{-1}$	$1.9 \times 10^{-2} \text{ min}^{-1}$	$3.9 \times 10^{-3} \text{ min}^{-1}$

Figure 1 P-polarized IRRAS spectrum of formate adsorbed on $\text{TiO}_2(110)$ surface ($\theta_{\text{HCOO}} = 0.5$). The symmetric and asymmetric $\nu_{\text{s,as}}(\text{OCO})$ vibrations are located at 1360 cm^{-1} and 1532 cm^{-1} , respectively, and the two $\delta(\text{C-H})$ bands at 1373 and 1388 cm^{-1} . The spectrum was recorded at 273 K . The crystal was aligned in the $[001]$ direction with respect to the plane of incidence of the IR beam.

Figure 2 IRRAS spectra of formate ($\theta_{\text{HCOO}} = 0.5$) adsorbed on TiO_2 (110) after different O_2 exposures times (between 0 and 150 minutes) and different pressures: (a) $P_{\text{O}_2} = 1 \times 10^{-6}$ mbar, (b) $P_{\text{O}_2} = 5 \times 10^{-7}$ mbar, (c) $P_{\text{O}_2} = 1 \times 10^{-7}$ mbar. The spectra were recorded at 273K with p-polarized light incident in the [001] direction.

Figure 3 IRRAS spectra of formate adsorbed on TiO₂(110) after different O₂ exposures (0, 10, 100, and 1000 L) prior to formic acid dosing ($\theta_{\text{HCOO}} = 0.5$). The spectra were recorded at 273K utilising p-polarized light incident in the [001] direction.

Figure 4 IRRAS spectra of formate adsorbed on TiO₂ (110) obtained at various times (0 – 180 minutes) after exposure of 100 L O₂ to the pristine rutile surface prior to dosing HCOOH to saturation coverage ($\theta_{\text{HCOO}} = 0.5$). The spectra were recorded at 273 K using p-polarized light incident in the [001] direction.

Figure 5 IRRAS spectra obtained at different times during H_2O dosing ($P_{\text{H}_2\text{O}}=7 \times 10^{-8}$ mbar) of a formate covered TiO_2 (110) surface ($\theta_{\text{HCOO}} = 0.5$). The spectra were recorded at 273K with p-polarized light incident in the [001] direction.

Figure 6 IRRAS spectra obtained with p-polarized light incident in the [001] direction, at various substrate temperatures (273 K, 303 K and 313 K) after exposure to 1000 L O₂ to the pristine rutile surface prior to dosing HCOOH to saturation coverage ($\theta_{\text{HCOO}} = 0.5$).

p-pol [001]

Figure 7 IRRAS spectra recorded with O_2 pressure $P_{O_2} = 1 \times 10^{-6}$ mbar at different times (0 – 180 minutes) after $HCOOH$ dosing ($\theta_{HCOO} = 0.5$), and at different substrate temperatures: (a) 273 K, (b) 303 K, (c) 323 K, and (d) 343 K. The spectra were recorded using p-polarized light incident in the [001] direction.

Figure 8 Formate (θ_A ; red) and bicarbonate (θ_X ; black) coverage deduced from the 1516 cm^{-1} (black) and 1532 cm^{-1} (red) absorbance bands as function of time at different substrate temperatures, (a) 273 K, (b) 303 K, (c) 323 K, and (d) 343 K. The absorbance bands were obtained by peak deconvolution of IRRAS spectra in Fig. 7. The solid lines are least-square fits to the experimental data using Eqns. 5 and 6.

Figure 9 Ball model of the rutile (110) surface showing the orientation of different formate species on surface; formate oriented parallel to the bridging oxygen rows and bonded to two Ti_{5c} atoms via the formate oxygen molecules (species A); formate bonded to a Ti_{5c} atom and a bridging oxygen vacancy site (species B), formate oriented along the [001] direction and bonded to an oxygen vacancy site and hydrogen bonded to bridging oxygen atom (species C); formate bonded to a Ti_{5c} atom and a hydroxylated oxygen vacancy site (species D). Also shown is the direction of the electric field for IR light incident along the [001] direction.

Figure 10. IRRAS spectra recorded with O_2 pressure $P_{O_2} = 1 \times 10^{-6}$ mbar at different times (0 – 150 minutes) after $HCOOH$ dosing ($\theta_{HCOO} = 0.5$) utilizing s-polarized light incident in the [001] direction.

Figure 11 IRRAS spectra obtained after long time exposure of a formate covered TiO_2 (110) surface ($\theta_{\text{HCOO}} = 0.5$) to UHV chamber background. Measurements were done at 303 K with p-polarized light incident in the [001] direction.

Figure 12 Arrhenius plot of the rate constant, k_r , (blue) for the reaction formate $\rightarrow$ surface bicarbonate species, and the removal rate, k_{des} , (red) for formate into gaseous species by desorption and dehydrogenation. The rate constant was determined at an O_2 pressure of $P_{O_2} = 1 \times 10^{-6}$ mbar using the deconvoluted peak area at 1516 cm^{-1} and 1532 cm^{-1} respectively, for the different species.