Fourier Transform Reflection−Absorption IR Spectroscopy Study of Formate Adsorption on TiO$_2$(110)

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The adsorption of the formate species produced by dissociative adsorption of formic acid on TiO$_2$(110) has been investigated using a combination of X-ray photoelectron spectroscopy (XPS) and Fourier transform reflection−absorption IR spectroscopy (FT-RAIRS). Adsorption at 300 K produces a formate coverage of 0.59 ML, in agreement with previous estimates and higher than that expected for a perfect (2 × 1) overlayer observed in low-energy electron diffraction (LEED). p-Polarized FT-RAIRS measurements carried out as a function of azimuthal angle (Φ) reveal the presence of two formate species through the coupling of both the tangential (I_t) and normal (I_n) components of the radiation to the symmetric (ν_{sym}(OCO)) and antisymmetric (ν_{asym}(OCO)) vibrational modes of the molecule. Species A has the OCO plane aligned in the $\langle 001 \rangle$ direction with C_{2v} symmetry; ν_{asym}(OCO) = 1566 cm^{-1} is observed as an absorption band (coupled to I_t) at Φ = 90°, and ν_{sym}(OCO) = 1363 cm^{-1}, observed as a transmission band (coupled to I_n). Species B has the OCO plane aligned in the $\langle 110 \rangle$ direction with C_s symmetry; ν_{asym}(OCO) = 1535 cm^{-1}, observed as an absorption band (coupled to I_t) at Φ = 0°, and ν_{sym}(OCO) = 1393 cm^{-1}, observed as a transmission band (coupled to I_n). Changes in the region of the ν_{sym}(OCO) at 1363 cm^{-1} for species A as a function of azimuthal angle (this band should be insensitive to Φ) are associated with an absorption band resulting from a coupling of ν_{sym}(OCO) of species B to I_t. This is a result of the reduction in symmetry from C_{2v} to C_s and, as expected from the adsorption geometry, is observed at Φ = 0° and not at Φ = 90°. We estimate that the coverages of species A and species B at 300 K are 0.4 and 0.2 ML, respectively. Species A is the adsorbate responsible for the formation of the (2 × 1) ordered structure and adsorbed between the TiO$_2$(110) oxygen rows. Species B we suggest is an adsorbed formate molecule with one of the oxygens incorporated in the TiO$_2$(110) oxygen rows and is the species associated with the so-called disordered phase. It is clear from FT-RAIRS that the coverage of species B is increased by adsorbing formic acid at higher surface temperatures. We suggest that species B adsorbs at defects (oxygen vacancies) created through dissociative adsorption of formic acid to produce species A and the subsequent reaction of two hydroxyl groups to produce water. The existence and interdependence of the two adsorbed formate species provide an explanation for the complex activity observed for various catalytic reactions of formic acid over titania.

Introduction

The adsorption and decomposition of formic acid on TiO$_2$(100),[1] TiO$_2$(001),[2] and TiO$_2$(110) single-crystal surfaces have received considerable attention. The widest variety of studies has been carried out on TiO$_2$(110), and the techniques applied include scanning tunneling microscopy (STM),[3,4] X-ray photoelectron spectroscopy (XPS),[5,6] photoelectron diffraction (PED),[7] low-energy electron diffraction (LEED),[6] temperature-programmed desorption (TPD),[8] and steady-state reaction studies.[6] Electronic structure calculations have also been performed[5] for annealed and defected surfaces.

Formic acid dissociatively adsorbs on TiO$_2$(110) at 250 K to form the formate species and adsorbed hydroxyl species. The formate produces an ordered (2 × 1) structure observed in LEED with a coverage of 0.5 ML (determined by XPS) on a stoichiometric surface (with coverage based on the number of 5-fold Ti^{4+} sites on the terraces of the clean surface).[6] The formate species is adsorbed on the terraces of the (1 × 1) surface, bridging two Ti^{4+} sites. The acid hydrogen atoms (or deuterium atoms when DCOOD is used) are proposed to adsorb on the bridging oxygen rows to form hydroxyl groups. Heating the formate-covered surface to 350 K results in recombinative

desorption of approximately 0.1 ML of the formate groups (recombination of formate and hydroxyl hydrogen) and desorption of water through disproportionation of bridging hydroxyl groups.[6] The (2 × 1) ordered LEED structure is lost at this temperature, leading to a so-called "disordered" phase. Heating to 400 K led to evolution of D$_2$, and this was again assigned to hydroxyl group recombination. Residual formate species unimolecularly decomposed at approximately 570 K to give a mixture of D$_2$, D$_2$O, DCOOD, CO, and CO$_2$.[6] The TiO$_2$(110) surface was found to catalyze both dehydrogenation (D$_2$ + CO$_2$) and dehydration (D$_2$O + CO) reactions, with the dehydrogenation products favored below 500 K, in contrast to the selective activity for dehydration that has been reported on TiO$_2$ powder catalysts.[6]

Other results[8] have suggested that the reactions of adsorbed formate on TiO$_2$(110) are not simple dehydrogenation and dehydration reactions but in fact involve a complex set of chemical processes including water formation, creation of oxygen vacancies, formation of formaldehyde, and facile exchange of lattice oxygen into formate. The importance of defects (oxygen vacancies) in the surface reactivity of TiO$_2$(110) with formic acid has been confirmed by the introduction of

defects by electron bombardment.[5] At 300 K the stoichiometric surface was found to adsorb ~0.58 ML of formate species (from XPS), although this was proposed to be in good agreement with the 0.50 ML expected for the (2 × 1) adsorbate layer. The defected surfaces were found to adsorb additional formate species, and the extra adsorption was found to be equal to half the number of extra defect sites (missing bridging oxygen atoms) created by electron bombardment. Electronic structure calculations[6] indicated that the bridging site proposed for the formate species in the (2 × 1) structure[6] was the most stable species on the stoichiometric surface. The adsorption configuration of the species associated with the (2 × 1) LEED structure on the stoichiometric surface has been further supported by STM studies[3,4] and photoelectron diffraction studies.[7] However, in the presence of defects in the bridging oxygen rows, a second formate species oriented at 90° with respect to the (2 × 1) species was proposed to be favorable,[5] with the formate bridging from one Ti^{4+} terrace site to between the two Ti^{3+} ions exposed by the removal of a bridging oxygen atom. A slight tilt from the horizontal was also proposed for this second formate species.

We have used the Fourier transform reflection−absorption IR spectroscopy (FT-RAIRS) technique to investigate the adsorption of the formate species on $TiO_2(110)$. The technique not only has the advantages of intrinsic resolution for surface vibrational spectroscopy but when carried out on a surface with a dielectric response of an insulator or semiconductor, FT-RAIRS can differentiate vibrational modes polarized both parallel and perpendicular to the surface normal. In addition, the azimuthal dependence of the parallel mode can be used to assess the orientation of the adsorbate.[9]

Experimental Section

Experiments were performed in an ultrahigh vacuum (UHV) chamber equipped with a mass spectrometer, LEED, XPS, and FT-RAIRS.[10,11] The $TiO_2(110)$ crystal was cleaned by cycles of argon ion bombardment at 800 K, annealing at 1000 K in UHV, and exposure to oxygen at 1×10^{-6} mbar during cooling to 400 K. Subsequent cooling to 300 K was allowed to take place without oxygen. LEED and XPS were used to verify that the periodicity was (1 × 1) and that the surface was clean with the minimum of defects, as one may expect under these conditions.[12,13] The formic acid was further purified and degassed by a number of freeze−thaw cycles under vacuum. p-Polarized FT-RAIRS spectra were recorded on a Perkin-Elmer 1720 using a mercury cadmium telluride (MCT) detector. Spectra were recorded at a resolution of 16 cm^{-1} by accumulation of 500 scans over approximately 3.5 min. A background scan was first recorded and subsequently subtracted from the scan taken following exposure of the surface to formic acid to produce the adsorbed formate species. The angle of incidence of the beam to the surface normal was 83° for all spectra presented. The azimuthal angle of incidence could be varied by a total of 120° using a sample goniometer. Although the spectral range accessible with the detector, window, and beam splitter combination was 700−4000 cm^{-1}, there was insufficient sensitivity to detect any vibrational modes associated with $\nu(C−H)$ of the adsorbed formate or $\nu(O−H)$ of adsorbed hydroxyl groups.

Results and Discussion

A series of FT-RAIRS spectra obtained as a function of exposure during the adsorption of formic acid on $TiO_2(110)$ at
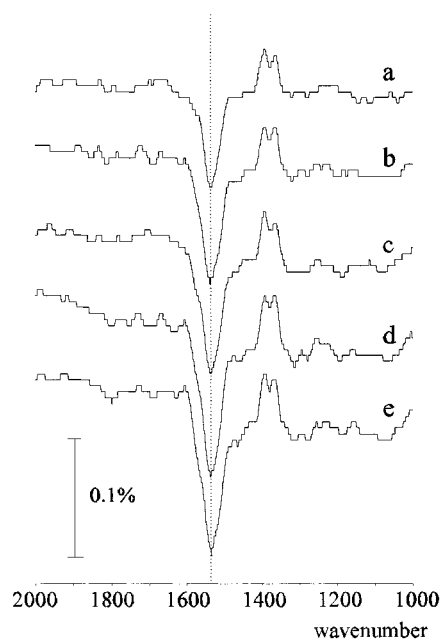

Figure 1. FT-RAIRS spectra obtained on exposing the $TiO_2(110)$ surface to formic acid at a surface temperature of 300 K: (a) 50 ML; (b) 200 ML; (c) 350 ML; (d) 500 ML; (e) 650 ML. The incident p-polarized radiation is incident at an azimuthal angle $\Phi = 90°$.

300 K are shown in Figure 1. The spectra are measured with the incident radiation aligned at an azimuthal angle $\Phi = 90°$ ($\Phi = 0°$ is defined as the $\langle 110 \rangle$ azimuth; see Figure 2). All spectra are characterized by two distinct vibrational features: an adsorption band at 1536 cm^{-1} and a transmission band (which consistently appears as a doublet; see below) centered at 1380 cm^{-1}. Neither of the bands appear to shift in frequency with coverage. The band at 1536 cm^{-1} we associate with $\nu_{asym}(OCO)$ of adsorbed formate, in line with the assignment on other oxide surfaces.[14] Coupling of this mode to the tangential component of the p-polarized radiation (I_t) is expected to result in an absorption band. The band at 1380 cm^{-1} we associate with $\nu_{sym}(OCO)$ of adsorbed formate, again in line with the assignment on other oxide surfaces[14] and HREELS results obtained for formate adsorbed on $TiO_2(110)$.[8] Coupling of this mode to the normal component of the p-polarized radiation (I_n) is expected to result in a transmission band. These results are consistent with the adsorption of a formate species (Figure 2) adsorbed with an orientation perpendicular to the surface plane, with the (OCO) bond aligned primarily along the $\langle 001 \rangle$ azimuth.[5−7] The formate species adsorbed on $TiO_2(110)$ at maximum coverage at 300 K is characterized by a C(1s) peak at 288.8 eV. Using the appropriate sensitivity factors[15] for C(1s) and Ti(2p), we estimate the maximum formate coverage to be 0.59 ML. This is slightly higher than that expected for the (2 × 1) formate structure but is consistent with previous XPS estimates of coverage for adsorption on the annealed $TiO_2(110)$ surface.[5]

The $\nu_{asym}(OCO)$ mode of adsorbed formate observed on $TiO_2(110)$ at 1536 cm^{-1} (Figure 1) is not observed in HREELS spectra,[8] while the $\nu_{sym}(OCO)$ mode at 1380 cm^{-1} is observed by both techniques. It is unlikely that this is due to a difference in the effective screening length associated with dipole scattering in HREELS for a mode polarized parallel to the $TiO_2(110)$ surface. Rather, it is a result of an unfortunate coincidence of a peak in the HREELS baseline spectrum at 1550 cm^{-1} resulting from inadequate deconvolution of the multiple phonon losses of the substrate.[16]
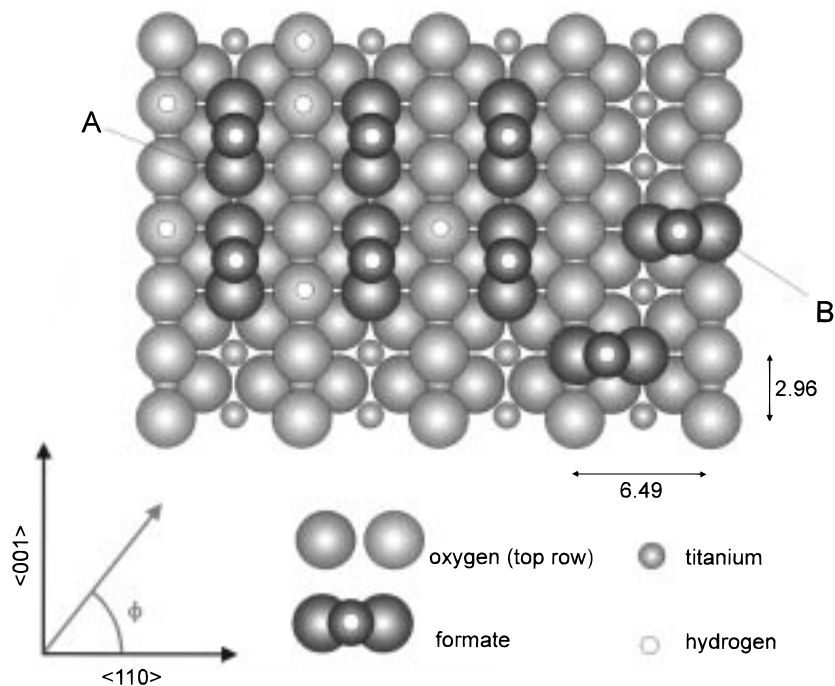
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Figure 2. Schematic showing the possible adsorption sites for formate species on TiO$_2$(110). Species A is suggested to be responsible for the (2 × 1) structure observed in LEED,[3-5,7] and species B forms at oxygen vacancies.[5] The azimuthal angle Φ of the incident p-polarized radiation is defined with $\Phi = 0°$ along the ⟨110⟩ direction. Note that the polarization of ν_{asym}(OCO) will be orthogonal for the two species and that the symmetry of species A and B are C_{2v} and C_s, respectively.
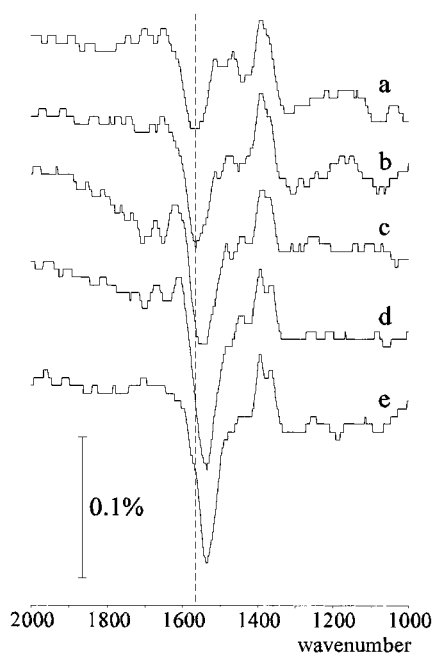

Figure 3. FT-RAIRS spectra obtained as a function of azimuthal angle Φ for formate on TiO$_2$(110) adsorbed at saturation coverage by exposure of the surface to formic acid at 300 K: (a) $\Phi = 0°$; (b) $\Phi = 15°$; (c) $\Phi = 30°$; (d) $\Phi = 60°$; (e) $\Phi = 90°$.

Figure 3 shows a series of FT-RAIRS spectra obtained as a function of the incident azimuthal angle for a TiO$_2$(110) surface dosed to saturation coverage of formate at 300 K. A systematic variation of the vibrational spectra is observed, but ν_{asym}(OCO), which couples to I_t, clearly does not reduce to zero intensity as one may have expected for a well-ordered (2 × 1) formate overlayer (Figure 2). Instead ν_{asym}(OCO) systematically shifts from 1535 cm^{-1} at $\Phi = 90°$ to 1566 cm^{-1} at $\Phi = 0°$ with a reduction of integrated intensity of ca. 50%. It should also be noted that the fwhm of ν_{asym}(OCO) increases at azimuthal angles

between $\Phi = 90°$ and $\Phi = 0°$, with the sharpest bands being observed for measurements along the high-symmetry directions. ν_{sym}(OCO), which couples to I_n, would not be expected to vary with Φ for a formate species oriented perpendicular to the TiO$_2$(110) surface. Indeed, ν_{sym}(OCO) with a band centered at 1380 cm^{-1} does not shift in frequency, or change in intensity, as a function of Φ (Figure 3). We note, however, a systematic change in ν_{sym}(OCO) (Figure 3) in that spectra taken at $\Phi = 90°$, consistently showing (see also Figure 1) a small splitting of the peak and a single peak at $\Phi = 90°$. We will return to this observation below.

The results of the azimuthal dependence of ν_{asym}(OCO) and ν_{sym}(OCO) can be understood in terms of the presence of two types of adsorbed formate species on the surface following the exposure of TiO$_2$(110) to formic acid at 300 K. On the basis of our XPS data, the total coverage of formate species at saturation coverage following adsorption at 300 K is 0.59 ML, in agreement with previous results.[5] Under these conditions we may therefore expect the additional coverage over and above that expected for species A in a (2 × 1) overlayer to be a result of the additional adsorption of species B (Figure 2); the introduction of oxygen vacancies by electron bombardment resulted in a concomitant increase in concentration of species B and total coverage.[5] Species A is associated with adsorption of formate within the row and is responsible for the (2 × 1) structure observed in LEED. The ν_{asym}(OCO) of this species would be expected to couple to I_t at $\Phi = 90°$, and there is no coupling expected at $\Phi = 0°$. The second, species B (Figure 2), has been suggested on the basis of electronic structure calculations.[5] Its azimuthal adsorption geometry is orthogonal to species A; the ν_{asym}(OCO) of this species would be expected to couple to I_t at $\Phi = 0°$, and there is no coupling expected at $\Phi = 90°$. The value of ν_{asym}(OCO) observed at $\Phi = 90°$ of 1566 cm^{-1} we therefore associate with species A, and ν_{asym}(OCO) observed at $\Phi = 0°$ of 1535 cm^{-1} is ascribed to species B. The value for ν_{sym}(OCO) of 1380 cm^{-1} is an average for the two species, although the apparent splitting of the transmission
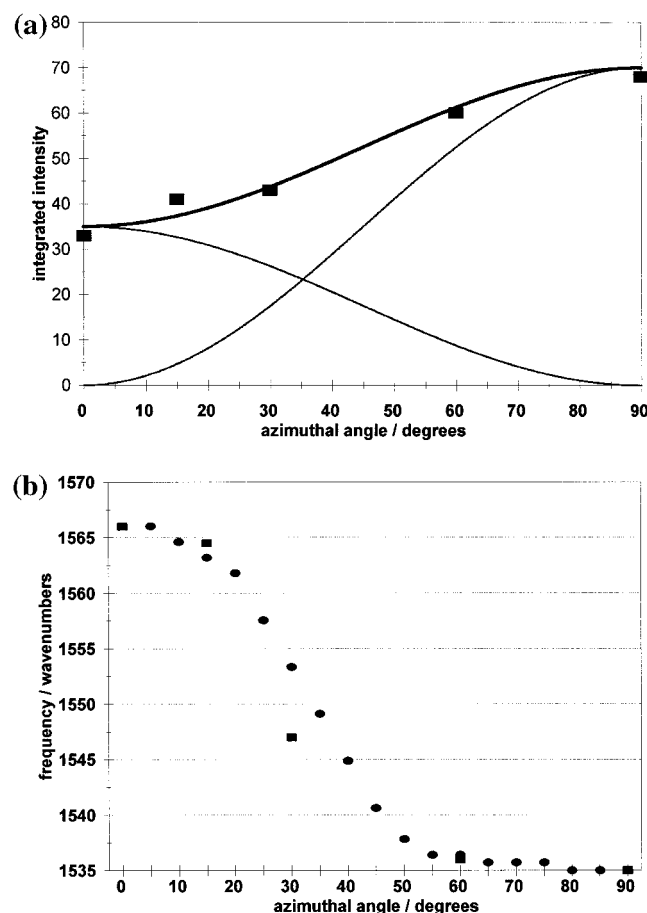
(a)

(b)

Figure 4. Measured (□) integrated intensity (a) and frequency (b) of the absorption band resulting from the coupling of I_t with $\nu_{asym}(OCO)$ as a function of azimuthal angle Φ together with the prediction assuming 0.4 ML of species A and 0.2 ML of species B. The measured peak is assumed to be composed of two Gaussian components at frequencies and with fwhm obtained from measurement at $\Phi = 90°$ and $\Phi = 0°$.

Figure 5. Schematic showing qualitatively the expected FT-RAIRS bands (in two azimuthal conditions) associated with $\nu_{asym}(OCO)$ and $\nu_{asym}(OCO)$ coupling to the tangential and normal components of the p-polarized radiation for species B (Figure 2), which has C_s symmetry (see text).

band may be associated with $\nu_{asym}(OCO)$ of the two different species. This possibility is discussed below with regard to the observed changes in the transmission band with azimuthal angle (Figure 3).

Assuming all Ti sites are coordinated to a formate species and assuming for each missing species A two adsorption sites are available for species B (Figure 2), we estimate the relative coverages of species A:B to be 0.4 ML:0.2 ML. Using the model described above to interpret the azimuthal dependence of the FT-RAIRS spectra (Figure 3), we are able to predict the integrated intensity and frequency dependence with Φ for the overlapping bands $\nu_{asym}(OCO)$ for the two species. Figure 4a shows the observed and predicted dependence of the integrated intensity of $\nu_{asym}(OCO)$ with Φ assuming that the absorption coefficients for the two species are the same. Figure 4b shows the observed and predicted dependence of the frequency of the peak maximum, assuming overlapping Gaussian peaks with the same relative fwhm to peak separation. Note that the predominance of species A shifts the rather sharp change in frequency to a lower range of azimuthal angle, as observed. Although these are not considered quantitative fits to the data, we suggest that the comparison provides qualitative evidence that our data are consistent with our model.

Because of the limited signal to noise, we dismissed the possibility that the transmission was actually made up of a $\nu_{sym}(OCO)$ doublet associated with the two formate species
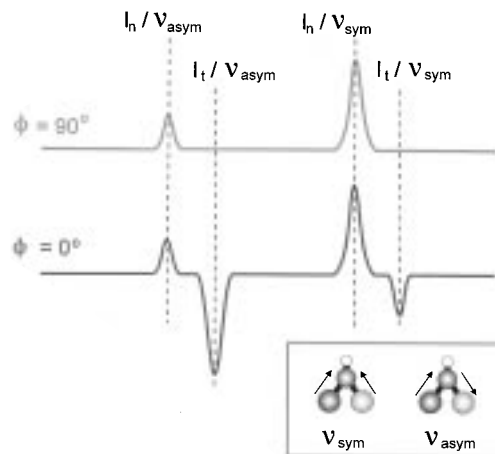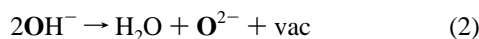
environments. However, the band was always observed over a large number of measurements[17] as a split feature for measurements at $\Phi = 90°$ and as a singlet at $\Phi = 0°$ (Figures 1 and 3). Since normal components of vibrational modes (coupling to I_n) should be invariant with Φ, it was difficult to account for the azimuthal dependence. It should be noted, however, that species B does not have C_{2v} symmetry but is reduced to C_s by incorporation of one of the formate oxygen atoms into the oxygen row (Figure 2). The effect of the removal of the reflection plane in C_{2v} perpendicular to the OCO bond to produce the C_s point group is to produce a parallel component to the $\nu_{sym}(OCO)$ mode and a perpendicular component to $\nu_{asym}(OCO)$ (both modes are fully symmetric in C_s). In addition, the perpendicular components of a mode will always be shifted to higher frequency with respect to the parallel components under this reflection geometry because of vibrational coupling contributions in the two-dimensional collective oscillator.[18–20] Coupling of I_t to the parallel component of $\nu_{sym}(OCO)$ for species B will be dependent on azimuthal angle. For the expected adsorption geometry (Figure 2), I_t would be expected to couple to the parallel component of $\nu_{sym}(OCO)$ at $\Phi = 0°$ and not at $\Phi = 90°$. Note that I_n would be expected to couple to the perpendicular component to $\nu_{asym}(OCO)$ at all angles Φ. The azimuthal dependence that one may expect for species B with C_s symmetry is summarized schematically in Figure 5. We suggest that the higher frequency component of the transmission feature (1393 cm^{-1}) is associated with the coupling of I_n to the perpendicular component of $\nu_{sym}(OCO)$ of species B. At $\Phi = 0°$ there is also a coupling of I_t to the parallel component of $\nu_{sym}(OCO)$ of species B. The latter is expected as an absorption band and shifted to slightly lower frequency. This band overlaps the $\nu_{sym}(OCO)$ of species A (the second component of the transmission feature at 1363 cm^{-1}), resulting in its disappearance at $\Phi = 0°$. At $\Phi = 90°$ there is no coupling of I_t to the parallel component of $\nu_{sym}(OCO)$ of species B, and hence, $\nu_{sym}(OCO)$ of species A is observed.

No additional transmission band is observed for the potential coupling of I_n with $\nu_{asym}(OCO)$, as would be predicted for species B in C_s configuration (Figure 5). The strength of the band will depend on the extent of the lowering of symmetry from C_{2v} imposed by the adsorption geometry to C_s, and we must assume that the band is insufficiently strong to be observed with the limited signal to noise of the measurement. The most stable configuration found from electronic structure calculations

for species B [5] was one in which the formate molecule exhibited a tilt in the ⟨110⟩ direction. This tilt would also contribute to the lowering of the symmetry of the molecule to C_s in the same way as that from incorporating one of the formate oxygen atoms in the TiO$_2$(110) rows. It is therefore difficult to assess the contribution of any molecular tilt to the apparent lowering of the symmetry measured using FT-RAIRS.

Although species B has not been previously observed explicitly at 300 K in STM[3,4] or photoelectron diffraction[7] studies, we suggest that the coverage above 0.5 ML expected for the perfect (2 × 1) overlayer (species A) observed here and elsewhere[5] is due to the adsorption of a smaller proportion of species B that we observed in FT-RAIRS. The adsorption of formate species B requires the existence, or creation, of surface defects (oxygen vacancies). We have no reason to believe from our previous work that the surface defect concentration following preparation of the clean stoichiometric surface is very high.[11] It is certainly not sufficiently high (0.2 ML) to account for our suggested coverage of species B. We suggest that the adsorption of species B results from the creation of defects through (1) the dissociative adsorption of formic acid to produce species A and surface hydroxyl species and (2) the recombination of hydroxyl groups to form water. If **O** represents a TiO$_2$(110) lattice oxygen, and **vac** a lattice oxygen vacancy, we can write

$$2HCOOH + 2\mathbf{O}^{2-} \rightarrow 2HCOO_A^- + 2\mathbf{OH}^- \qquad (1)$$

$$2\mathbf{OH}^- \rightarrow H_2O + \mathbf{O}^{2-} + vac \qquad (2)$$

This process has been suggested previously to compete with the recombinative desorption of formic acid on the basis of TPD and electron elastic scattering experiments on TiO$_2$(110);[8] water desorption following dissociative adsorption of formic acid on TiO2(110) takes place in the temperature range 275−500 K. In addition, a reduction in the elastic reflectivity of electrons in the temperature range 250−400 K is associated with defect (**vac**) formation. This would suggest that reactions 1 and 2 can take place at 300 K, the adsorption temperature used here. We suggest that once created, the defect site is available for the adsorption of species B:

$$HCOOH + \mathbf{O}^{2-} + vac \rightarrow 2HCOO_B^- + \mathbf{OH}^- \qquad (3)$$
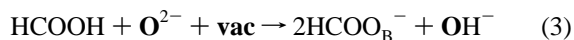
A test of this thesis, and a confirmation of the assignment of the bands observed to the two formate species, was made by carrying out the adsorption of formic acid at a higher surface temperature, a condition where the creation of defects through hydroxyl recombination and the desorption of water would be more extensive, since the processes of hydroxyl recombination (reaction 2) is activated. Figures 6 and 7 show FT-RAIRS spectra taken following exposure of the TiO$_2$(110) surface to formic acid (to saturation coverage) at 300 K (part a) and 450 K (part b). This is below the temperature at which decomposition of formate is observed in TPD.[8] Measurements are made at $\Phi = 90°$ (Figure 6) and $\Phi = 0°$ (Figure 7). Figure 6 shows that the absorption band (coupling of I_t) previously associated with ν_{asym}(OCO) of species A decreases in intensity through adsorption at higher temperature. Concomitantly, Figure 7 shows an increase in intensity for the absorption band (coupling of I_t) previously associated with ν_{asym}(OCO) of species B. Note also that the intensity of the transmission band associated with coupling of I_n to ν_{sym}(OCO) of species A at 1363 cm^{-1} also appears to have been reduced. Since this is not reflected in spectra obtained at $\Phi = 90°$ (Figure 6), we suggest it is again due to an increasing interference of an absorption band due to
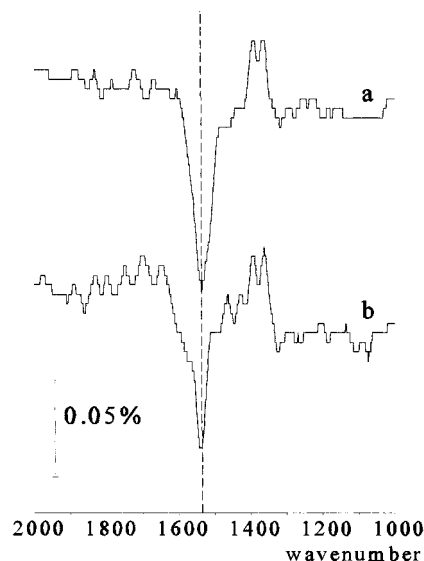

Figure 6. FT-RAIRS spectra taken following exposure of the TiO$_2$(110) surface to formic acid (to saturation coverage) at 300 K (a) and 450 K (b). Measurements are made at $\Phi = 90°$.
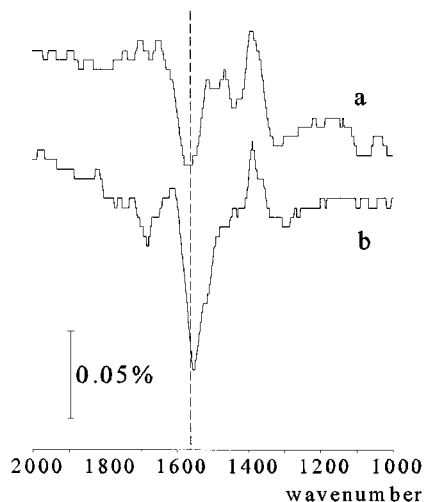

Figure 7. FT-RAIRS spectra taken following exposure of the TiO$_2$(110) surface to formic acid (to saturation coverage) at 300 K (a) and 450 K (b). Measurements are made at $\Phi = 0°$.

ν_{sym}(OCO) of species B (coupling to I_t) rather than to the reduced intensity expected for ν_{sym}(OCO) of species A. These observations are clearly in agreement with our assignment to two distinct species of adsorbed formate and with the observation that the formation of the species B is promoted by the creation of oxygen defects. In addition, the adsorption of species B excludes the adsorption of species A.

Species A and species B are likely to be responsible for the two distinct decomposition pathways observed on this surface.[8] The two activation barriers (52 and 75 kJ mol^{-1}) observed for the overall dehydration reaction to produce CO we associate with species A and species B, respectively. Species B is also responsible for the isotopic mixing in the dehydration product associated with the higher activation barrier and is likely to be the species responsible for an alternative branching of the reaction to produce formaldehyde and CO$_2$. The two species could also be responsible for the dehydration (species B) and dehydrogenation (species A) reactions observed under different conditions.[6] Since an ensemble of vacancies is probably required for the reaction of species B to produce formaldehyde and CO$_2$,[2] ensembles of hydroxy species favor the creation of **vac** (1) over

recombinative desorption, and since the dehydration reaction of species A and B will result in the net removal of **vac**, one should expect the branching ratio of species B to produce various products to be highly dependent on reaction conditions.

The explanation of why species B has not previously been observed explicitly at 300 K in STM[3,4] or photoelectron diffraction[7] studies is probably because the reaction of species A to form the required defects is just beginning around this temperature, and hence, it is the minority species. It is possible that at just slightly lower temperatures pure species A can indeed be produced. Unfortunately, we were not able to stabilize the FT-RAIRS measurements sufficiently with a cooled manipulator to verify this suggestion. In addition, coadsorption of the parent molecule (formic acid) is observed below about 250 K, complicating the interpretation of the formate FT-RAIRS spectra.

Conclusions

The adsorption of the formate species produced by dissociative adsorption of formic acid on $TiO_2(110)$ has been investigated using a combination of XPS and FT-RAIRS. This has allowed the identification of two formate species, which can be formed on $TiO_2(110)$ through the dissociative adsorption of formic acid.

Adsorption at 300 K produces a formate coverage of 0.59 ML, estimated from XPS results. This is higher than the coverage expected for a perfect (2×1) overlayer observed in LEED but is in agreement with previous estimates. p-Polarized FT-RAIRS measurements of the adsorbate layer formed at 300 K have been carried out as a function of azimuthal angle (Φ). All spectra are characterized by two features. The first is an absorption band resulting from the coupling of the antisymmetric ($\nu_{asym}(OCO)$) vibrational mode of formate to the tangential component of the radiation (I_t); this mode is polarized primarily parallel to the surface plane. The second is a transmission band(s) resulting from the coupling of the symmetric ($\nu_{sym}(OCO)$) vibrational mode of formate to the normal component of the radiation (I_n); the mode is polarized primarily normal to the surface plane.

The azimuthal-dependent measurements reveal the presence of two different formate species that are adsorbed orthogonally to each other on the surface. Species A has the OCO plane aligned in the $\langle 001 \rangle$ direction with C_{2v} symmetry; $\nu_{asym}(OCO)$ = 1566 cm^{-1} is observed as an absorption band (coupled to I_t) at $\Phi = 90°$, and $\nu_{sym}(OCO)$ = 1363 cm^{-1} is observed as a transmission band (coupled to I_n).

Species B has the OCO plane aligned in the $\langle 110 \rangle$ direction with C_s symmetry; $\nu_{asym}(OCO)$ = 1535 cm^{-1} is observed as an absorption band (coupled to I_t) at $\Phi = 0°$, and $\nu_{sym}(OCO)$ = 1393 cm^{-1} is observed as a transmission band (coupled to I_n). Changes in the region of the $\nu_{sym}(OCO)$ at 1363 cm^{-1} for species A as a function of azimuthal angle (this band should be insensitive to Φ) are associated with an absorption band resulting from a coupling of $\nu_{sym}(OCO)$ of species B to I_t. This is a result of the reduction in symmetry from C_{2v} to C_s and, as expected from the adsorption geometry, is observed at $\Phi = 0°$ and not at $\Phi = 90°$.

The coverages of species A and species B at 300 K are estimated to be 0.4 and 0.2 ML, respectively, on the basis of the FT-RAIRS measurements and in agreement with our suggested adsorption model. Species A is the adsorbate responsible for the formation of the (2×1) ordered structure and adsorbed between the $TiO_2(110)$ oxygen rows. Species B we suggest is an adsorbed formate molecule with one of the oxygens incorporated in the $TiO_2(110)$ oxygen rows. This species has previously been suggested to be the most likely structure on the defective surface.[5] Species B requires the formation of an oxygen vacancy defect that takes place through dissociative adsorption of formic acid to produce species A and surface hydroxy species, and the recombination of hydroxy species to produce water. It is clear from the FT-RAIRS that the coverage of species B is increased by adsorbing the formic acid at higher surface temperatures where defect creation is favored. The clear spectroscopic identification of two formate species on TiO2(110) and the suggested mechanism by which they form provide a basis for understanding the complex catalytic reactivity of formic acid over titania surfaces.

References and Notes

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