

Structure determination of formic acid reaction products on TiO₂(110)

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The (110) face of the rutile phase of TiO₂ is perhaps the most-studied of oxide surfaces (e.g. [1, 2]), in part because while perfect stoichiometric crystals are insulators, typical crystals of this material used in surface science experiments have a significant number of bulk defects (oxygen vacancies and/or titanium interstitials) creating a semiconductor which is moderately conducting; this makes these surfaces amenable to study by the wide range of electron spectroscopic techniques. In addition, of course, there is considerable practical interest in TiO₂ surfaces as a support of metal particles in heterogeneous catalysis and as a photocatalytic oxidiser. Despite this, in common with other oxide surfaces, there are very few quantitative structural studies of adsorbates on this surface. On this model surface there has been significant interest in its interaction with formic acid which produces a (2x1) surface phase [3] associated with deprotonation of the acid to create adsorbed formate, HCOO- [4], and this system has been investigated by quite a wide range of techniques. An earlier O 1s photoelectron diffraction investigation of this surface [5, 6] (including chemical-state specificity) showed that the small amount of data collected were consistent with an adsorption geometry found in total energy calculations, notably with the formate species is aligned along the [001] bridging an adjacent pair of surface 5-fold-coordinated Ti atoms with the formate O atoms near-atop the Ti atoms, but did not include a true experimental structure determination.

Using chemical-state specific scanned-energy mode photoelectron diffraction (PhD) from the O 1s and C 1s photoemission we have conducted a full determination of the local structure of the surface species produced on the rutile TiO₂(110) surface as a result of room temperature exposure to formic acid. The results show clear evidence for the coexistence of coexistent formate, HCOO-, and hydroxyl, OH. The formate species occupies the same site favoured by the earlier photoelectron diffraction study, the O atoms being near-atop 5-fold-coordinated Ti surface atoms with a Ti-O bondlength of 2.08±0.03 Å, also consistent with STM observations and a number of theoretical calculations. The hydroxyl species are formed by H attachment to the surface bridging O atoms and have a Ti-O bondlength of 2.02±0.05 Å, significantly longer than for the bridging oxygen atoms on a bulk-terminated surface or as previously reported for the clean surface. Our results exclude the possibility of a large (30%) fractional occupation by the formate species of a second site azimuthally rotated by 90° and bonded to a surface oxygen vacancy site, as proposed in some earlier infrared and X-ray absorption spectroscopic studies. A much smaller concentration of such a second species could, however, be present. A notable feature of our results is that while the location of adsorbed H on surfaces is extremely difficult to determine by any method, in the present case the influence of the adsorbed H atom can be established through the determination of the geometry of the O atom in the adsorbed OH species.

References

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