# A theoretical study of $HCO_2H$ adsorption on $TiO_2(110)$

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This paper presents calculations (CRYSTAL program) on the interaction of formic acid with models for the (110) face of the rutile $TiO_2$ structure. $HCO_2H$ strongly dissociates on the surface leading to a formate anion. Thus, the best adsorption mode results from an acidic cleavage contrary to what would be expected from the comparison of the basic and acidic gas-phase cleavages. This occurs since the adsorbed $HCO_2^-$ is stabilized as a bidentate species; the adsorption involves two oxygen atoms bound to two surface titanium atoms.

**Keywords:** adsorption, Hartree–Fock, oxide, formic acid

## 1. Introduction

$TiO_2$ is an amphoteric oxide; the exposed metallic cations are the acidic sites and the oxygen atoms at the surface are the basic sites. The selectivity in the catalytic decomposition reaction of carboxylic acids and alcohols has been used as a probe [1] of the acid–base properties. Fragments resulting from the decomposition are acidic and basic species adsorbed on the different sites of the surface. Several investigations have already studied the interaction of formic acid on $TiO_2$ [2–4], MgO [5–7], and ZnO [8,9] single-crystal surfaces. These studies have shown that formic acid adsorbs dissociatively to form adsorbed formates, $HCO_2^-$, and surface hydroxyl groups.

$HCO_2H$ has two basic oxygen atoms; the oxygen from the carbonyl group is more basic than that of the hydroxyl group. The molecular adsorption can involve each of these oxygen atoms independently, or both of them simultaneously. The dissociative adsorption implies the cleavage of the OH bond (acidic cleavage) or that of the OC bond (basic cleavage). Referring to heterolytic cleavages, it leads to the adsorption of a couple of ions or another: a formate ion and a proton for the acidic cleavage or $HCO^+$ and $OH^-$ for the basic cleavage. The resulting adsorption modes correspond to different orientations of the adsorbed fragments since the anion, formate or hydroxyl, goes on the titanium sites whereas the cation, $HCO^+$ or $H^+$ goes on the oxygen sites.

Calculations are performed using an ab initio Hartree–Fock crystalline orbital method (the CRYSTAL program [10,11]).

This paper is organised in the following way. We first present the isolated molecule and the $TiO_2$ (110) surface. Next, we analyse the various adsorbed structures resulting from the molecular and dissociative adsorption. The heats of adsorption for all the adsorption modes are gathered in table 1. Finally, we investigate the possibilities of fragmentation of the formic acid on the surface.

## 2. The formic acid molecule

The geometry optimisation for formic acid is performed with the MONSTERGAUSS program [12] using the PS-31G basis set for carbon and oxygen atoms, and the 31G basis set for the hydrogen atom. This optimisation yields the parameters shown on figure 1 in agreement with experimental [13] data.

The proton is oriented toward the C=O (trans); the opposite conformation (cis) is less stable by 7.7 kcal/mol. An adsorption that involves both oxygen atoms

Table 1
Heat of adsorption (kcal/mol) at $\theta = 1$ ($\theta = 1/2$ in parentheses)

| | Adsorption on the polymer | Adsorption on the (110) surface |
|---|---|---|
| *molecular adsorption* | | |
| monodentate through carbonyl group | 32.1 | 58.5 (65.0) |
| monodentate through OH group | 26.2 | 48.6 (57.6) |
| 1M-bidentate structure | no adsorption | no adsorption |
| 2M-bidentate structure | (44.2) | (68.6) |
| *dissociative adsorption* | | |
| basic cleavage | 51.9 | 104.7 (132.6) |
| acidic cleavage | | |
| 1M-monodentate structure | 44.7 | 69.0 (95.7) |
| 1M-bidentate structure | 6.3 | 61.9 (80.0) |
| 2M-bidentate structure | (103.0) | (174.0) |

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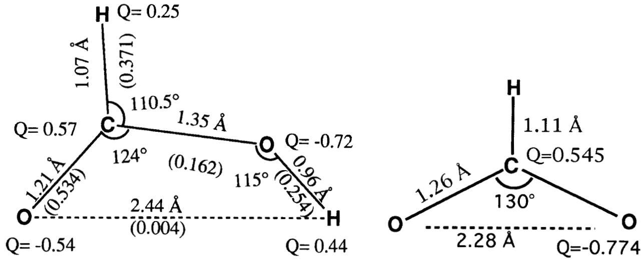


Figure 1. Optimized bond distances and angles for trans-formic acid (HCOOH) at the left-hand side (the experimental data are C=O = 1.202 Å, C–O = 1.343 Å, O–C–O = 124.9°, O–H = 0.972 Å, H–O–C = 106.3°, C–H = 1.097 Å, H–C–O = 124.1°) and for the formate ion ($HCOO^-$) at the right-hand side. Mulliken overlap populations are in parentheses.

requires to rotate the proton away from the surface and hence has to overcome the 7.7 kcal/mol energy loss.

Formic acid is known to be dimerised; the energy of dimerisation, 18.7 kcal/mol calculated at the PS-31G level (14.1 experimental [14]) has not been taken into account for the evaluation of the heats of adsorption and would reduce them.

When molecularly adsorbed, the formic acid coordinates to the cation and behaves as a base. This was the case for all the adsorbates that we have considered on $TiO_2$. The binding through a H-bond, where the formic acid would be an acid is weak. Formic acid has two basic sites, the oxygen from the carbonyl and that from the hydroxyl group. According to the proton affinities, the carbonyl oxygen is the most basic site:

$$\begin{aligned} &\mathrm{HCOOH} + \mathrm{H}^+ \to \mathrm{HC(OH)}_2^+ \\ &\quad \Delta H = -184.1\ \mathrm{kcal/mol} \\ &\quad (\mathrm{exp.}\ [15] = -182.8\ \mathrm{kcal/mol}), \\ &\mathrm{HCOOH} + \mathrm{H}^+ \to \mathrm{HCOOH}_2^+ \\ &\quad \Delta H = -166.6\ \mathrm{kcal/mol}. \end{aligned}$$

The larger proton affinity of the carbonyl group is explained by the coordination; the carbonyl oxygen atom is singly-coordinated (even if it is through a double bond) and thus more reactive than the oxygen atom from the hydroxyl which has two neighbors. The level of the highest occupied molecular orbital (HOMO), mainly localised on the oxygen pair of the carbonyl group exhibits this difference. Mesomerism also explains the affinity order: $HC(OH)_2^+$ can be represented by two resonant structures while $HCOOH_2^+$ must localise one electron pair on the O atom of $OH_2^+$. In contrast, the charges on the oxygen atoms (large for the hydroxyl) and the Mulliken overlap populations (large for C=O) would lead to the wrong conclusion. The electrons on the oxygen atom of the hydroxyl group are stabilized by the field of the neighbours and not very reactive.

In the gas phase, the CO bond cleavage, “basic cleavage”, of formic acid is more favorable than the OH bond cleavage, “acidic cleavage”.

$$\begin{aligned} &\mathrm{HCOOH} \to \mathrm{OH}^- + \mathrm{HCO}^+ \\ &\quad \Delta H = 290.6\ \mathrm{kcal/mol} \\ &\quad (\mathrm{exp.}\ [16] = 259\ \mathrm{kcal/mol}), \\ &\mathrm{HCOOH} \to \mathrm{HCOO}^- + \mathrm{H}^+ \\ &\quad \Delta H = 356.7\ \mathrm{kcal/mol} \\ &(\mathrm{exp.}\ [17] = 345.2\ \mathrm{kcal/mol}). \end{aligned}$$

The formation of the formate ions, $RO^-$ (R = HCO) and $H^+$ appears to be less favorable than that of the formyl ions, $R^+$ and $OH^-$; these results are similar to those obtained for methanol (R = $CH_3$); however, in the case of $HCOO^-$, the presence of two oxygen atoms increases the possibilities of stabilization by adsorption. In the gas phase, the formyl cation, $HCO^+$, is linear. It is a protonated form of carbon monoxide, more stable [18] than $COH^+$.

## 3. The polymer and slab models

We have used two models for the adsorption of formic acid over the rutile (110) surface: a polymer and a slab.

Our polymer representing the rutile surface is the main building block of the rutile. It is a chain containing the linear sequence of titanium atoms and the equatorial oxygen atoms attached to them. This polymer can be obtained by the cleavage of all the apical Ti–O bonds of the rutile structure that are the weakest bonds (see figure 2); thus, the polymer contributes to the main part of the relative stability of the various $TiO_2$ surfaces [19]. It presents two sites of adsorption, tetracoordinated titanium sites that are acidic and bridging oxygen sites that are basic. The presence of tetracoordinated cations does not create states in the band gap and the electronic structure remains close to that of larger systems. This polymer has been used to study the adsorption of other molecules [20–24]; hence, the adsorption of the formic acid may be compared with those of a variety of different adsorbates.

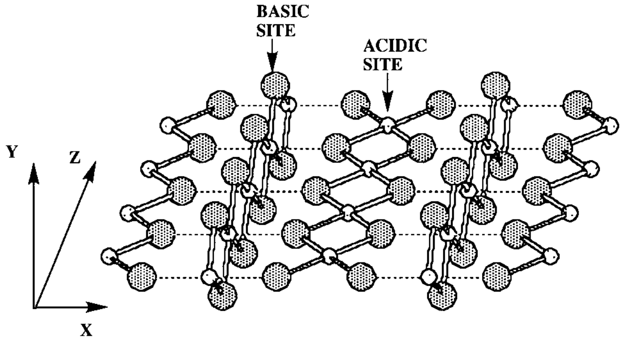


Figure 2. The slab model for the (110) face. The polymer model appears by the breaking of all the apical TiO bonds (dotted lines). These dative bonds imply a donation from the horizontal polymers (in the *xz* plane) to the vertical ones (in the *yz* plane).

The slab model for the (110) surface is the top layer that results from the coupling of polymers along the $x$ direction by dative bonds. Half of the polymers are in the surface plane ($xz$ plane) whereas the others are perpendicular ($yz$ plane, see figure 2). The dative bonds generate a charge transfer of 0.056 $e$ from the horizontal polymers to the vertical ones. A consequence is that the tetracoordinated titanium atoms are very charged and therefore the (110) face is very acidic. For other adsorbates, this extra reactivity represents a factor two [25], 90%, 130% and 160% for $CO_2$, $H_2O$ and $NH_3$ respectively. Since the (110) face is the most dense one and since the top layer has no dipole moment, the (110) face is stable and can be obtained by crystal cleavage without reconstruction [26]. The cohesive energy of the top layer of the (110) face calculated with 25 $k$-points in the irreducible Brillouin zone, is 118 kcal/mol per $TiO_2$ unit (an improvement of 35 kcal/mol relative to the polymer). These two models correspond to perfect surfaces assuming no defect and no reconstruction. It is established that the structure of $TiO_2$ surfaces are similar to those of the bulk [27–29].

The adsorption energies have been calculated according to the expression:

$$E_{\mathrm{ads}} = E_{\mathrm{HCOOH}} + E_{\mathrm{TiO_2}} - E_{(\mathrm{HCOOH/TiO_2})}\,,$$

where $E_{(\mathrm{HCOOH/TiO})_2}$ is the total energy of the adsorbate/substrate system, $E_{\mathrm{TiO_2}}$ is the total energy of the substrate and $E_{\mathrm{HCOOH}}$ is the total energy of the isolated adsorbate in its equilibrium geometry (trans conformation). A positive $E_{\mathrm{ads}}$ value corresponds to a stable adsorbate/substrate system.

## 4. The molecular adsorption of HCOOH

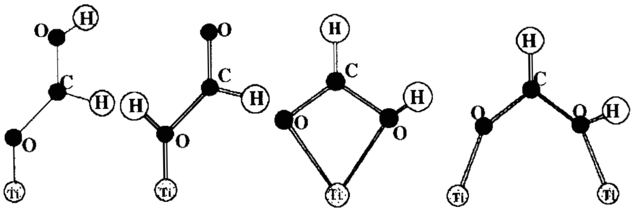
We have investigated four configurations for molecularly adsorbed formic acid on $TiO_2$ surface: monodentate bound through the carbonyl group, monodentate bound through the hydroxyl group, 1M-bidentate and 2M-bidentate (see figure 3).

### *4.1. One adsorbed function, the monodentate adsorption*

#### *4.1.1. Adsorption through the carbonyl group*

In the case of the polymer, the adsorbate is oriented in the $xy$ plane perpendicular to the axis of the polymer with the hydroxyl group down so that the proton interacts with the surface oxygen atoms by a weak H-bond (the H···O distance is 2.66 Å). The adsorption energy is positive (32.1 kcal/mol). Such adsorption mode cannot be transferred to the (110) slab because of the repulsion between the OH group and the oxygen atoms of the adjacent polymer. Then, the hydroxyl group is oriented upwards (figure 4). The increase of the heat of adsorption (see table 1) is due to the increased acidity of the titanium site in the (110) face (see section 3).

The orientation along the polymer axis ($yz$ plane) is favorable when the OH is oriented down; then it leads to the 2M-bidentate (see section 4.2.2).



monodentate through the carbonyl group | monodentate through the hydroxyl group | 1M-bidentate structure | 2M-bidentate structure

Figure 3. The adsorption modes for molecular adsorption.

#### *4.1.2. Adsorption through the hydroxyl group*

For hydroxyl adsorption, the carbonyl group is oriented away from the surface to prevent repulsion with the oxygen atoms from the surface (figure 4). The heat of adsorption (table 1) is smaller than for the carbonyl adsorption as expected from the proton affinities (see section 2).

The adsorption energy for the slab (table 1) is again larger than that on the polymer. The C–OH bond is weakened under adsorption with an elongated distance, 1.42 Å (1.35 Å in the molecule), and a very negative overlap population, suggesting an easy basic cleavage for the adsorbate.

### *4.2. Two adsorbed functions, 2M-bidentate structure (bridging structure)*

No stable structure has been found for the 1M-bidentate conformation.

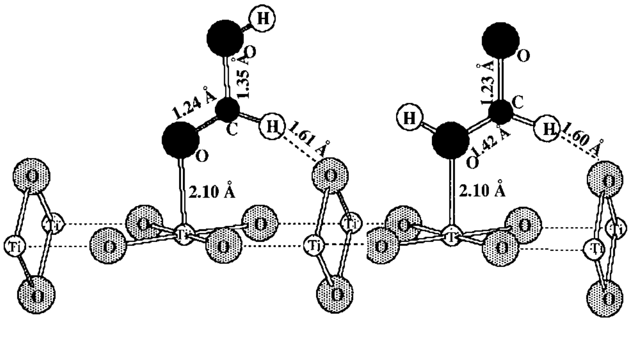


Figure 4. The optimised parameters of molecular adsorption of the formic acid through the carbonyl group (right-hand side) and the hydroxyl group (left-hand side) on the (110) face. For the adsorption through the carbonyl group, the hydroxyl group is oriented away from the surface. The H from CH is positively charged ($Q = +0.43$) and bound to the surface oxygen by an important H-bond (OP=0.097). The CH and the C–OH bond are weakened (OP(CH)=0.147 vs. 0.371, OP(CO)=0.110 vs. 0.162 in figure 1). The C=O is nearly unchanged, this adsorption mode could be a precursor to the decomposition leading to CO and $H_2O$. For the adsorption through the hydroxyl group, the H from CH is positively charged ($Q = +0.46$) and bound to the surface oxygen by a H-bond (OP=0.054).

In the 2M-bidentate conformation, the two oxygen atoms of the formic acid are bound to different Ti atoms from the surface. The adsorption energy (see table 1) is much larger than for the adsorption through one oxygen atom. The optimized structure is shown in figure 5. The oxygen from the carbonyl group is more strongly bound to the surface than the oxygen from the hydroxyl group in spite of nearly similar distances; this appears on the Mulliken overlap populations (0.039 vs. 0.025 respectively).

## 5. The dissociative adsorption of formic acid

In spite of the name "acid", the easiest dissociation of formic acid in the gas phase is a basic cleavage (see section 2). This suggests a basic cleavage on the surface leading to the following orientation: $HCO^+$ on $O(TiO_2)$ and $OH^-$ on $Ti(TiO_2)$. In table 1, it is shown that the adsorption mode occurs dissociatively; basic cleavage is found as long as we consider the adsorption of only one oxygen atom.

### *5.1. Basic cleavage*

The basic cleavage case with the $OH^-$ group bound to the titanium atom is favorable. On the polymer at saturation, the formyl groups, $HCO^+$, are oriented perpendicularly to the polymer in order to prevent repulsion with the adjacent adsorbed species. The $OH^-$ groups are oriented to allow a sequence of H-bonds (with an $OP = 0.017$), along the polymer axis, $z$. Such orientation is found for the water adsorption [21]. At lower coverage, this repulsion between the adsorbates vanishes and the $HCO^+$ groups prefer to be in the polymer plane.

For the (110) face, the formyl groups, $HCO^+$, are oriented perpendicularly to the polymer. The $OH^-$ groups are also perpendicular to the polymer axis allowing a H-bond with the formyl group ($O \cdots H = 1.77$ Å, with an $OP = 0.027$). This is better than when the $OH^-$ groups form a chain along the polymer axis ($O \cdots H = 2.16$ Å, with an $OP = 0.018$ for the H-bonds). At lower coverage, the H-bond between the $OH^-$ and the $HCO^+$ groups is increased ($OP = 0.041$) and the perpendicular orientation is still the best (at $\theta = 1/2$, $E_{ads} = 132.6$ kcal/mol vs. $E_{ads} = 118.8$ kcal/mol when $OH^-$ and $HCO^+$ are oriented along the polymer axis). This strong H-bond contributes to produce a large adsorption energy on the (110) face; it nearly doubles (see table 1) relative to the polymer model. The optimized parameters are presented on figure 6. In table 1, dissociation to formyl is not the most favorable case. Formyl does not seem to be experimentally observed. This is also true on metal surfaces [30,31]. $HCO^+$ being a protonated form of CO, it should easily decompose to CO and $H^+$; the decomposition on the (110) surface is exothermic by 17 kcal/mol.

Note that our reasoning associates the distribution of the fragments on the surface to the heterolytic cleavage. An homolytic cleavage ($HCOOH \rightarrow HCO\cdot + OH\cdot$) would produce neutral fragments and would lead to a different distribution ($HCO\cdot$ would go on the metal [32]). Results of calculation (the HCO fragment goes on the oxygen site) therefore justifies the electron count associated with the heterolytic cleavage even if we do not claim to access to a mechanism.

### *5.2. The acidic cleavage*

The acidic cleavage leads to the formate anion (figure 1) and the proton $H^+$. Once adsorbed on the titanium oxide surface, the formate anion is bound to the titanium atom and the proton to the bridging oxygen. On the $TiO_2$ (110) surface, the formate ion can be adsorbed in three different configurations: a monodentate structure in which one oxygen atom of the formate is coordinated to a surface cation via a single O–Ti bond, a 1M-bidentate structure and a 2M-bidentate structure (or bridging structure) (figure 7).

#### *5.2.1. One function adsorbed, the monodentate structure*

This mode seems arbitrary since the geometry seems favorable to a 2M-bidentate structure when the formate is oriented along the axis of the polymer. To have 1M-

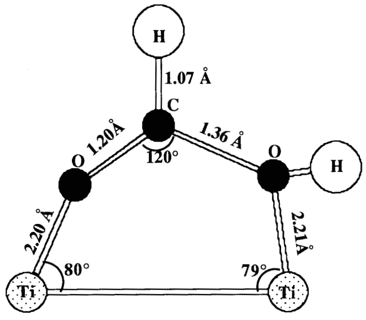


Figure 5. The optimised geometric parameters for formic acid on $TiO_2$.

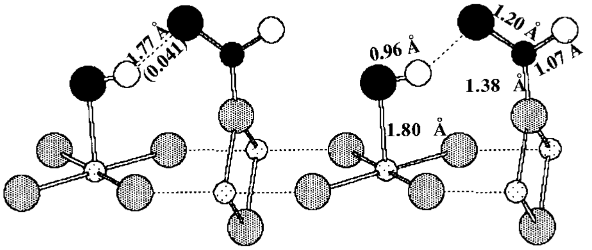


Figure 6. The optimised bond distances and angles for formic acid with basic cleavage on the $TiO_2$ (110) surface at $\theta = 1/2$. C and O atoms for HCO are represented in black (small circles for C) and H atoms are in white. The $O \cdots H$ bond distances for the H-bonds are indicated with the overlap population in parentheses.

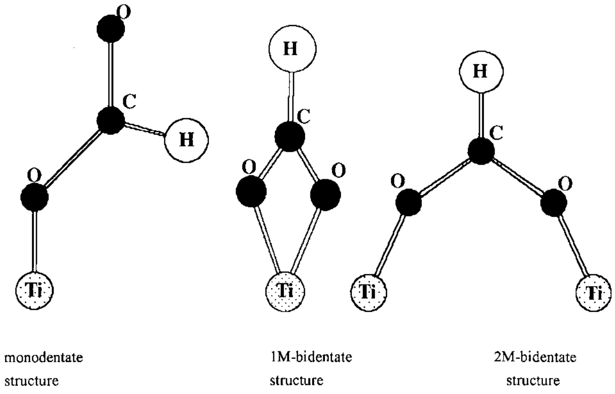


Figure 7. The adsorbed configurations of formate species.

monodentate requires to avoid the interaction of the carbonyl with the adjacent Ti site; thus the carbonyl has to be oriented upward, away from the adjacent Ti. The situation may be different on other oxides with larger metal–metal distances. The O–O distance in the formate, 2.28 Å (see figure 1), is short and the bridging mode requires the metal–metal distance to be small [4]. The bridging mode is favorable when the M–M distances are 2.98, 3.0 and 3.18 Å in MgO(100) [6,7], $TiO_2(110)$ [4] and ZnO(10$\bar{1}$0) [33] respectively. In contrast, the monodentate coordination is preferred on the (0001)-Zn surface of ZnO [8,34,35] where Zn–Zn=3.25 Å and on $ZrO_2(100)$ [36] where Zr–Zr = 3.64 Å, the increase of the O–C–O angle would be too large.

On the polymer model, the singly-coordinated formate anion is in the plane $xy$ perpendicular to the polymer plane and the unbound oxygen atom is oriented towards the surface, stabilised by H-bonding with the proton adsorbed (the H···O distance is 2.29 Å and the OP 0.009; the stabilisation represents 6.25 kcal/mol). On the slab model, the oxygen atom is oriented upward, away from the surface plane in order to prevent the repulsion with the oxygen atoms from the perpendicular polymer. The adsorption energy is inferior to that for the basic cleavage in agreement with the gas-phase cleavages (see section 2). The situation is very similar to that for the methanol adsorption [24]; the CO bond cleaves more easily than the OH bond.

### 5.2.2. *Two functions adsorbed on one metal site, the 1M-bidentate structure*

In the 1M-bidentate structure, the two equivalent oxygen atoms from the $HCO_2^-$ group are bound to one titanium center. The adsorption energy, very small on the polymer, is more important on the slab (110). Besides the high reactivity of this face (see discussion in section 3), the formate ion benefits from two H-bonds with the adsorbed protons. This adsorption mode is, however, not competitive with other modes (table 1).

### 5.2.3. *Two functions adsorbed on two metal sites, the 2M-bidentate structure*

This is the most stable system. It has been experimentally determined on the (110) face [4] at temperature between 180 and 230 K. This is also the best adsorption mode on many transition metal surfaces, Mo [37,38], Ru [39], Rh [40], Ni [41], Pd [42], Pt [43], Cu [44–46] and on $(HCOO)_4Cu_2(NCS)_2$ cluster [47]. According to the metal the dissociation of the formic acid may be endothermic or exothermic. Shustorovich [48] has calculated the activation barriers of different signs. The formate is always adsorbed with the $\eta^2$ coordination, or 2M-bidentate structure [37,49]. Formate may be generated from several routes starting from methanol or formaldehyde at low temperature on ZnO [9] or on transition metal catalysts [50].

On $TiO_2$, the adsorption energy is larger than for any other mode (see table 1), exceeding the sum of those for the 1M-monodentate (dissociative adsorption) and the monodentate through the carbonyl group (molecular adsorption). The optimised geometry for this structure is symmetrical and remains very close to that of the formate ion in the gas phase (compare figure 9 with figure 1) in spite of an important TiO bonding (OP = 0.078); relative to the formate anion in the gas

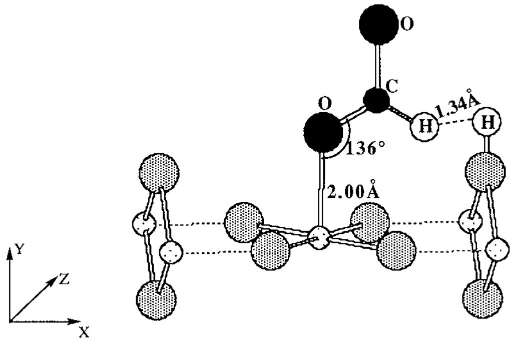


Figure 8. Dissociative adsorption of formic acid with one function adsorbed at $\theta = 1$. The HH distance is short but does not generate a strong repulsion since the charge of H in the formate is nearly zero; the HH overlap population is weakly negative, −0.018.

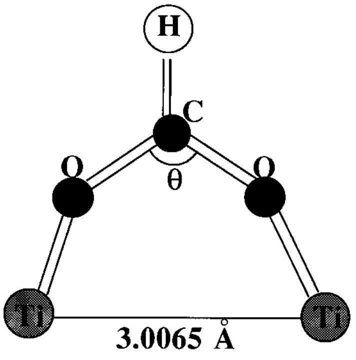


Figure 9. The 2M-bidentate formate anion; on the slab $d_{CO} = 1.26$ Å, $\theta = 127°$ and $d_{TiO} = 2.15$ Å and on the polymer $d_{CO} = 1.27$ Å, $\theta = 126°$ and $d_{TiO} = 2.03$ Å.

phase, the CO bond is weakened (0.318 vs. 0.414). The increase in reactivity when the result on the slab is compared with that on the polymer, 69%, is inferior to those for more basic adsorbates, $NH_3$ or $H_2O$ [25].

This adsorption mode is general for other carboxylic acids; the heat of adsorption of the acetic acid is 112.1 kcal/mol and 182.3 kcal/mol on the polymer and the slab respectively. These values are comparable with those of table 1 (slightly larger). The large adsorption value is due to the use of two functions. Dicarboxylic acids have more possibilities; indeed, for the oxalic acid [23] the best adsorption mode corresponds to the oxalate adsorption with two oxygens adsorbed from the two acidic groups. The adsorption that involves the two oxygen atoms from the same acidic group (that of the hydrogen oxalate) is also important even if the substituent effect of the $CO_2H$ group leads to a value slightly smaller than that of the formic acid.

## 6. Decomposition of formic acid

The best adsorption mode found so far is dissociative. Then, the question is raised of a more drastic decomposition of the formic acid on the surface. At high temperature, it decomposes. This has been observed since 1911 [51]. According to Onishi et al. [4] the decomposition of formates is "popular on metal oxides" [52] and, on the $TiO_2(110)$ surface, the decomposition is complete at 570 K to leave the clean surface and a mixture of CO, $CO_2$, $H_2$, $H_2O$ and $HCO_2H$ [3,4,53]. On other surfaces [2,36], $H_2CO$ is also formed; it is not observed on Ti(110). The local coordination around the reaction sites is supposed to control the decomposition [4]. Ti(110) favors dehydrogenation below 600 K, contrasting with other $TiO_2$ catalysts [3]. Formate ions also decompose on metal surfaces [48]. In contrast, on transition metal complexes the reverse reactions are known. Formic acid is the reaction product [50,54].

### 6.1. Gas-phase decomposition

The fragments may be inferred from the thermodynamics of the gas-phase reactions. Formally, formic acid can decompose according to the following processes:

$$HCOOH \rightarrow CO + H_2O \quad \Delta H_{calc.} = +6.9 \text{ kcal/mol}$$

($\Delta H_{calc.} = +4.1$; kcal/mol when the molecules resulting from the dissociation interact),

$$HCOOH \rightarrow CO_2 + H_2 \quad \Delta H_{calc.} = +13.7 \text{ kcal/mol}$$

($\Delta H_{calc.} = +12.7$ kcal/mol when the molecules resulting from the dissociation interact). The reaction that leads from one result to the other is the water–gas shift reaction. The first reaction takes place on acidic oxides whereas the second one, an oxidation–reduction reaction that generates carbon dioxide is associated to basic oxides [1,3]. From $CO_2$, one can obtain bicarbonate and carbonate species in the presence of water.

A third reaction, disproportionation, leads to the formation of formaldehyde,

$$2HCOOH \rightarrow CO_2 + H_2CO + H_2O$$
$$\Delta H_{calc.} = +12.5 \text{ kcal/mol}.$$

Calculated enthalpies show that these reactions are nearly athermic. With the PS-31G basis sets, they are found to be slightly endothermic at variance with the similar decomposition for oxalic acid [23]; the endothermicity would be more pronounced if the acid was initially dimerised. At the MP2/631G* level [55], the enthalpies are −5.1, +15.2 and +8.2 kcal/mol respectively.

### 6.2. Decomposition on the $TiO_2$ surface

In order to estimate the enthalpies of these reactions on the slab, we need the adsorption energies of each product, $H_2$, $H_2O$, $H_2CO$, $CO_2$, CO calculated independently on the slab at $\theta = 1/2$ (table 2). $H_2O$ adsorbs dissociatively [21]. At $\theta = 1/2$, CO [22] and $CO_2$ [56] molecules adsorb in upright position above Ti atoms. Hydrogen is dissociatively adsorbed, a proton on the outmost oxygen atoms and a hydride on the exposed titanium atom at 2.2 Å. $H_2CO$ adsorption is dissociative; $HCO^-$ is adsorbed on the Ti site through the carbon atom and a proton is adsorbed on the O site. The sum of the adsorption energies of the products, $E_{ads}(CO/TiO_2 + H_2O/TiO_2)$=161.4 kcal/mol, $E_{ads}(CO_2/TiO_2 + H_2/TiO_2)$=110.2 kcal/mol and $\frac{1}{2}E_{ads}(CO_2/TiO_2 + H_2CO/TiO_2 + H_2O/TiO_2) = 132.2$ kcal/mol are inferior to that of formic acid so that the decomposition of formic acid is not facilitated by adsorption on the oxide. A similar conclusion was reached for the oxalic acid [23].

Table 2
Heat of adsorption of the various compounds resulting from the decomposition of formic acid on the (110) face. For $H_2$, the adsorption is dissociative with one hydrogen atom bound to a surface oxygen and the other to the metal [63,64]. The molecular adsorption on the titanium center is very weak, 2.2 kcal/mol, and that on the oxygen center is slightly endothermic. $H_2CO$ adsorption is dissociative; the molecular adsorption only represents 33.8 kcal/mol. $HCO^-$ is adsorbed through the carbon atom; this is better than through the oxygen atom by 37 kcal/mol contrary to calculated results on MgO [32] where HOC binds through oxygen to Mg

| Adsorbed system | Adsorption energies (kcal/mol) |
|---|---|
| $H_2O_{diss}$ | 136.2 |
| CO | 25.2 |
| $CO_2$ | 36.1 |
| $H_{2diss}$ | 74.1 |
| $HCOOH_{diss}$ | 174. |
| $H_2CO_{diss}$ | 92.0 |

$$\mathrm{HCOOH/TiO_2} \rightarrow \mathrm{CO/TiO_2} + \mathrm{H_2O/TiO_2} \qquad \Delta H_{\mathrm{calc.}} = +19.5\ \mathrm{kcal/mol}, \tag{1}$$

$$\mathrm{HCOOH/TiO_2} \rightarrow \mathrm{CO_2/TiO_2} + \mathrm{H_2/TiO_2} \qquad \Delta H_{\mathrm{calc.}} = +77.5\ \mathrm{kcal/mol}, \tag{2}$$

$$2\mathrm{HCOOH/TiO_2} \rightarrow \mathrm{CO_2/TiO_2} + \mathrm{H_2CO/TiO_2} + \mathrm{H_2O/TiO_2} \qquad \Delta H_{\mathrm{calc.}} = +96.2\ \mathrm{kcal/mol}. \tag{3}$$

The first reaction appears to be the most likely decomposition. The coadsorption of water and carbon monoxide can produce formic acid (reverse reaction (1)). "Similar reaction has been postulated on MgO. On non-reducible oxide surfaces oxygen can only be introduced into reacting molecules by the reaction with adsorbed basic $OH^-$ groups, e.g. reduction of CO on MgO surfaces [57]".

The second reaction is an oxidoreduction on the surface. The $H_2$ adsorption is weak since the binding of H to a titanium atom is not very favorable. According to Raupp and Dumesic [58,59] "the titania surfaces are evidently incapable of dissociating significant amounts of molecular hydrogen". $H_2$ adsorbs and dissociates mainly at defects sites on $TiO_2(110)$ [27]. We therefore conclude that the decomposition of the formate does not proceed by the formation of adsorbed hydrogen (hydride) on the Ti site. The decomposition should arise differently from a favourable coupling of the H (proton) adsorbed on an oxygen site with the H of the formate (removed as an hydride, but never adsorbed on a titanium site). Bringing together the two H to 1.34 Å has been found not too repulsive for the 1M monodentate species at $\theta = 1$. This mechanism is different from that proposed by Noto et al. [60]. A possible motion is a tilt of the formate as proposed on $ZnO(10\bar{1}0)$ [33], MgO(001) [7] and $ZrO_2(100)$ [36] with a geometry even more favorable (see figure 10). The tilt is destabilizing by 5–18 kcal/mol for tilt angles in the range 30°–60°; this represents 3–10% decreases for the heat of adsorption. It raises to 42 kcal/mol for a 90° tilt. Next, a migration of the proton hydroxyl appears weakly destabilizing: a motion that keeps the OH distance constant and orients the proton toward the hydrogen of the formate (the OH is tilted by 24° and rotated) costs 9.2 kcal and leads to a $H\cdots H$ distance of 1.77 Å associated with a positive overlap population (see figure 11). This intermediate remains more stable than $CO_2/TiO_2 + H_2/TiO_2$ by 26.3 kcal/mol.

On $TiO_2$ the decomposition leading to dehydrogenation is less favorable than on MgO, which is more basic. The estimate for MgO to be compared with reaction (2) is less endothermic:

$$\mathrm{HCOOH/MgO} \rightarrow \mathrm{CO_2/MgO} + \mathrm{H_2} \qquad \Delta H_{\mathrm{calc.}} = +13.4\ \mathrm{kcal/mol}. \tag{2b}$$

On MgO the heats of adsorption are weaker; dihydrogen is not adsorbed; the $CO_2$ adsorption is strong relatively to other adsorbates and thus the endothermicity of the decomposition is weak.

Hydrogenation of $CO_2$ to formic acid (reverse reaction (2)) is known experimentally using late-transition-metal complexes as homogeneous catalyst [50,54] and has been the subject of theoretical analysis [61]. This does not seem to occur on metal oxides.

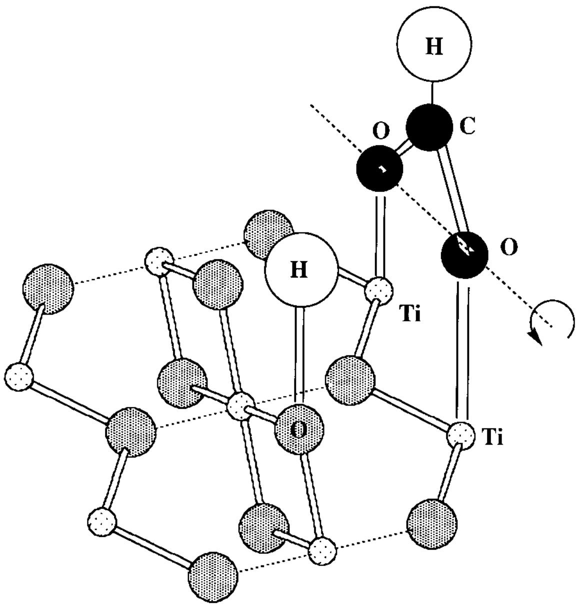


Figure 10. The tilt motion of the adsorbed formate; this motion brings the hydrogen atoms close to each other.

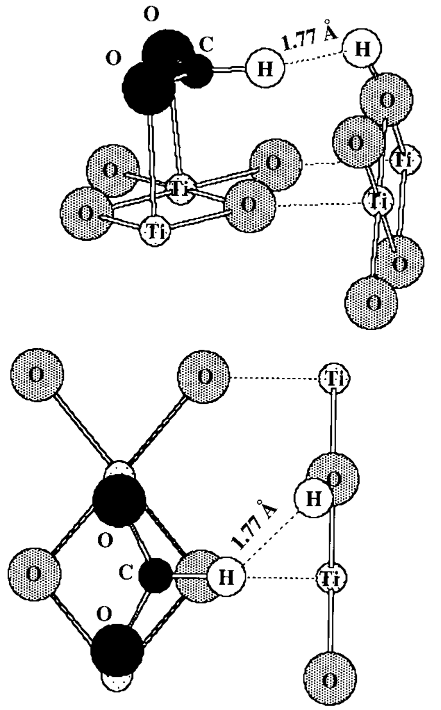


Figure 11. The calculated intermediate for tilt of the formate and the orientation of the proton hydroxyl toward the formate. View in perspective and top view.

On $TiO_2$(110), the third reaction does not seem to be possible due to the weakness of the heat of adsorption of the formaldehyde.

## 7. Summary

On the $TiO_2$ (110) surface, formic acid is found to cleave on the clean (110) surface. Despite the trends for the gas-phase cleavages (the acidic cleavage is less favorable than the basic cleavage), the formate ion is formed. The main reason is that the adsorption involves both oxygen atoms of the formate: the formate ion is strongly adsorbed as 2M-bidentate species in agreement with the experimental results [62]. The molecular adsorption, which is less favorable, also involves two different adsorption sites. This observation seems to have a general character: when the adsorbate can involve several sites of adsorption without excessive distortion to adapt its geometry, this leads to the optimal situation; in the co-adsorption of water and ammonia, ammonia is similarly bound to the surface by three bonds [25]. The comparison of the result on the slab with that on the polymer shows a 69% increase. The relative increase is rather moderate compared with other molecules but represents an absolute increase similar to that of $NH_3$ [25]. This high reactivity of the (110) face is due to an enhanced acidity of the titanium sites already found for $H_2O$ and $NH_3$. For the same adsorption modes, heats of adsorption at $\theta = 1/2$ are 30% larger than at $\theta = 1$. The comparison between the various adsorption modes is unaffected by the coverage.

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## References

[1] P. Mars, J.J.F. Scholten and P. Zwietering, Adv. Catal. 14 (1963) 35.
[2] K.S. Kim and M.A. Barteau, Langmuir 6 (1990) 1485.
[3] H. Onishi, T. Aruga and Y. Iwasawa, J. Am. Chem. Soc. 115 (1993) 10460.
[4] H. Onishi, T. Aruga and Y. Iwasawa, J. Catal. 146 (1994) 557.
[5] W.T. Petrie and J.M. Vohs, Surf. Sci. 259 (1991) L750.
[6] M.A. Szymanski and M.J. Gillan, Surf. Sci. 367 (1996) 135.
[7] H. Nakatsuji, M. Yoshimoto, M. Hada, K. Domen and C. Hirose, Surf. Sci. 336 (1995) 232.
[8] W.T. Petrie and J.M. Vohs, Surf. Sci. 245 (1991) 315.
[9] J.M. Vohs and M.A. Barteau, Surf. Sci. 176 (1986) 91.
[10] R. Dovesi, C. Pisani, C. Roetti, M. Causa and V.R. Saunders, CRYSTAL (Indiana University, Indiana, 1988).
[11] C. Pisani, R. Dovesi and C. Roetti, in: *Lecture Notes in Chemistry*, Vol. 48 (Springer, Berlin, 1988).
[12] R.A. Poirier and M. Peterson, MONSTERGAUSS (Newfoundland, Canada, 1989).
[13] G.H. Kwei and R.F. Curl, J. Chem. Phys. 32 (1960) 1592.
[14] W. Waring, Chem. Rev. 51 (1952) 171.
[15] D.H. Aue and M.T. Bowers, in: *Gas Phase Ion Chemistry*, Vol. 2, ed. M.T. Bowers (Academic Press, New York, 1979) p. 1.
[16] K. Hiraoka and P. Kebarle, J. Am. Chem. Soc. 99 (1977) 366.
[17] J.E. Bartmess and R.T.J. McIver, in: *Gas Phase Ion Chemistry*, Vol. 2, ed. M.T. Bowers (Academic Press, New York, 1979) p. 87.
[18] Y. Yamagushi, C.A. Richards Jr. and H.F. Schaefer III, J. Chem. Phys. 101 (1994) 8945.
[19] P. Reinhardt and B.A. Hess, Phys. Rev. B 50 (1994) 12015.
[20] J. Ahdjoudj, A. Fahmi and C. Minot, in: *The Synergy between Dynamics and Reactivity at Clusters and Surfaces*, Vol. 465, ed. L.J. Farrugia (Kluwer Academic, Dordrecht, 1995) p. 257.
[21] A. Fahmi and C. Minot, Surf. Sci. 304 (1994) 343.
[22] A. Fahmi and C. Minot, J. Organomet. Chem. 478 (1994) 67.
[23] A. Fahmi, C. Minot, P. Fourré and P. Nortier, Surf. Sci. 343 (1995) 261.
[24] J. Ahdjoudj, A. Fahmi and C. Minot, Surf. Sci. 352–354 (1996) 529.
[25] A. Markovits, J. Ahdjoudj and C. Minot, Surf. Sci. 365 (1996) 649.
[26] V.E. Henrich, Rep. Prog. Phys. 48 (1985) 1481.
[27] V.E. Henrich and R.L. Kurtz, Phys. Rev. B 23 (1981) 6280.
[28] M. Tsukada, H. Adachi and C. Satoko, Prog. Surf. Sci. 14 (1983) 113.
[29] T. Wolfram, J. Vac. Sci. Technol. 18 (1981) 428.
[30] N.D.S. Canning and R.J. Madix, J. Phys. Chem. 88 (1984) 2437.
[31] J.E. Crowell, J.G. Chen and J.T. Yates, J. Chem. Phys. 85 (1986) 3111.
[32] S.A. Pope, I.H. Hillier, M.F. Guest, E.A. Colbourn and J. Kendrick, Surf. Sci. 139 (1984) 299.
[33] H. Nakatsuji, M. Yoshimoto, Y. Umemura, S. Takagi and M. Hada, J. Chem. Phys. 100 (1996) 694.
[34] W.T. Petrie and J.M. Vohs, Surf. Sci. Lett. 274 (1992) L503.
[35] J. Jupille and N.V. Richardson, Surf. Sci. Lett. 274 (1992) L501.
[36] P.A. Dilara and J.M. Vohs, J. Chem. Phys. 97 (1993) 12919.
[37] S.L. Miles, S.L. Bernasek and J.L. Gland, Surf. Sci. 127 (1983) 271.
[38] C. Xu and D.W. Goodman, J. Phys. Chem 100 (1996) 1753.
[39] N.R. Avery, B.H. Toby, A.B. Anton and W.H. Weinberg, Surf. Sci. 122 (1982) L574.
[40] F. Solymosi, J. Kiss and I. Kovacs, J. Phys. Chem. 92 (1988) 796.
[41] R.J. Madix, J.B. Gland, G.E. Mitchell and B.A. Sexton, Surf. Sci. 125 (1983) 481.
[42] C. Egawa, I. Doi, S. Naito and K. Tamaru, Surf. Sci. (1986) 491.
[43] P. Hoffmann, S.R. Bare, N.V. Richardson and D.A. King, Surf. Sci. 133 (1983) L459.
[44] B.A. Sexton, Chem. Phys. Lett. 65 (1979) 469.
[45] B.A. Sexton, Surf. Sci. 88 (1979) 319.
[46] D.P. Woodruff, C.F. McConville, A.L.D. Kilcoyne, T. Lindner, J. Somers, M. Surman, G. Paolucci and A.M. Bradshaw, Surf. Sci. 201 (1988) 228.
[47] D.M.L. Goodgame, N.J. Hill, D.F. Marsham, A. Skapski, M.L. Smart and P.G.H. Troughton, J. Chem. Soc. Chem. Commun. (1969) 629.
[48] E. Shustorovich, Adv. Catal. 37 (1990) 101.
[49] T.S. Jones, N.V. Richardson and A.W. Joshi, Surf. Sci. 207 (1988) L948.
[50] A. Behr, *Carbon Dioxide Activation by Metal Complexes* (VCH, Weinheim, 1988).

[51] A. Mailhe and P. Sabatier, Compt. Rend. Acad. Sci. 151 (1911) 1212.

[52] W.D. Peng and M.A. Barteau, Catal. Lett. 7 (1990) 395.

[53] Y. Yamaguchi, H. Onishi and Y. Iwasawa, J. Chem. Soc. Faraday Trans. 91 (1995) 1663.

[54] F. Gassner, E. Dinjus, H. Görls and W. Leitner, Organomet. 15 (1996) 2078.

[55] N. Hertz, G. Rasul and G.A. Olah, J. Am. Chem. Soc. 115 (1993) 1277.

[56] A. Markovits, A. Fahmi and C. Minot, J. Mol. Struct. THEOCHEM (1996).

[57] R.A. van Santen, in: *World Scientific Lecture and Course in Chemistry*, Vol. 5, ed. S.H. Lin (World Scientific, Singapore, 1991) p. 331.

[58] G.B. Raupp and J.A. Dumesic, J. Phys. Chem. 89 (1985) 5240.

[59] W. Göpel, G. Rocker and R. Feierabend, Phys. Rev. B 28 (1983) 3427.

[60] Y. Noto, K. Furuda, T. Onishi and K. Tamaru, Trans. Faraday Soc. 63 (1967) 3081.

[61] F. Hutschka, A. Dedieu and W. Leitner, Angew. Chem. Int. Ed. Engl. 34 (1995) 1742.

[62] H. Onishi and Y. Iwasawa, Chem. Phys. Lett. 226 (1994) 111.

[63] G.L. Griffin and J.T. Yates, J. Chem. Phys. 77 (1982) 3751.

[64] A.B. Anderson and J.A. Nichols, J. Am. Chem. Soc. 108 (1986) 4742.