Theoretical Study of the Chemisorption and Surface Reaction of HCOOH on a ZnO(10$\bar{1}$0) Surface

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The mechanisms of the molecular and dissociative adsorption of formic acid HCOOH on a ZnO(10$\bar{1}$0) surface were investigated by means of the *ab initio* molecular orbital method using a Zn_4O_4 cluster embedded in an electrostatic field represented by 464 point charges at the crystal ZnO lattice positions. *cis*-Formic acid molecularly adsorbs on a ZnO(10$\bar{1}$0) surface without activation energy. It dissociates into a formate anion $HCOO^-$ and a proton H^+ with an activation energy of 11.7 kcal/mol. The formate anion is geometrically stable in the bridging structure of two Zn atoms and the unidentate structure of a Zn atom interacting with a surface OH species. The adsorption energy is about 80 kcal/mol for both structures. In contrast, the bidentate structure is about 24 kcal/mol less stable. Possible reaction pathways for the dissociation of the O−H bond of *cis*-formic acid were also examined. *trans*-Formic acid is dissociatively adsorbed on a ZnO(10$\bar{1}$0) surface to form a formate anion and a surface OH species without activation energy. The initial formate anion generated from *trans*-formic acid continues to interact with the surface OH species. This interaction produces the stability of the unidentate structure. Interconversion between the unidentate and bridging structures was also examined. The formate anion can be easily tilted on the surface by a small perturbation, leading to increased interaction between the formate species and the surface.

1. Introduction

Metal oxides are good catalysts for a variety of chemical processes as well as good supports for catalysts.[1−23] For example, the decomposition of methanol, formaldehyde, or formic acid readily occurs on ZnO catalysts.[1−6] In various water gas shift reactions on the surfaces of metal oxides,[12−15] such as MgO, Al_2O_3, and ZnO, the formate anion has been suggested to be a surface intermediate. Formic acid is adsorbed dissociatively on metal and metal oxide surfaces at room temperature to give the formate anion and surface hydroxyl species.[4−6,10,16−23] Three structures have been suggested for the formate anion adsorbed on metal oxide surfaces:[4−6,10,16−23] bridging, bidentate, and unidentate structures as shown in Figure 1. Noto *et al.* studied the dissociative adsorption and decomposition of formic acid on a ZnO surface using infrared spectroscopy, and the structure of the formate ion adsorbed on a ZnO surface was considered to be either bridging or bidentate.[3] Au *et al.* reported that formic acid is adsorbed on a ZnO(10$\bar{1}$0) surface and gives the formate anion and hydroxyls.[4] Petrie and Vohs studied the adsorption and reaction of formic acid on the (0001)-Zn surface of ZnO. They reported that molecularly adsorbed formic acid is the major species at 160 K, and it dissociates into the unidentate formate anion by heating.[5]

Formic acid adsorbed on metal and metal oxide surfaces decomposes to produce H_2O + CO or H_2 + CO_2.[1−6,11−23] Many studies have been performed to clarify the active species, the mechanism of the reactivity, and the selectivity of the catalysts in the decomposition reaction of formic acid.
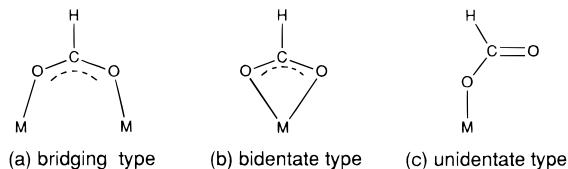

Figure 1. Three possible geometries for the formate anion on the surface.

Theoretical studies have been conducted on hydrogen chemisorption on a ZnO surface[24,25] and on the surfaces of other metals and metal oxides[26−33] to investigate the nature of the active sites, the structure of the adsorbed species, and the route and mechanism of the surface reaction. In a previous theoretical study, we examined the adsorption of formic acid and surface reactions on the MgO(001) surface.[34] In this paper, we report a theoretical study of the molecular and dissociative adsorption of formic acid on a ZnO(10$\bar{1}$0) surface. The crystal structures of MgO and ZnO are of the NaCl and wurtzite types, respectively. MgO is an insulator, whereas ZnO is a semiconductor. These differences cause differences in reactivity, selectivity, and surface properties. We compared the mechanisms of the reactions on a ZnO(10$\bar{1}$0) surface to those on an MgO(001) surface.

The model for the ZnO surface and the calculation method used in this work are described in Section 2. In the gas phase, *trans*-formic acid is calculated to be more stable than *cis*-formic acid by 6.4 kcal/mol, and the energy barrier between them is calculated to be 5.6 kcal/mol relative to the *cis* form. This suggests that formic acid in the gas phase is a mixture of both forms. Therefore, we should consider that both *trans* and *cis* forms approach the surface from the gas phase. The adsorption of *cis*- and *trans*-formic acids is described in sections 3 and 4, respectively. The structure of the adsorbed formate anion, which

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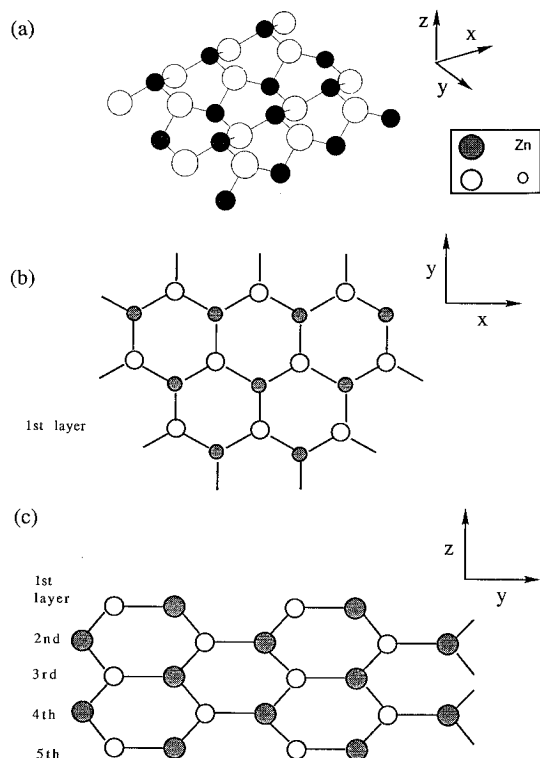
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Figure 2. Structure of the wurtzite ZnO crystal lattice: (a) whole view of the ZnO wurtzite crystal lattice; (b) view from above the ZnO(10$\bar{1}$0) surface; (c) side view of the ZnO wurtzite crystal lattice.

Figure 3. Zn$_4$O$_4$ cluster as a model of the ZnO(10$\bar{1}$0) surface. This cluster is taken from the first, second, and third layers of the ZnO crystal lattice and is placed in an electrostatic field represented by 464 point charges located in the ZnO crystal lattice. The first layer of the Zn$_4$O$_4$ cluster is used for the adsorption and dissociation of HCOOH. The arrows indicate the sites of adsorption for the formate anion in the bridging and bidentate forms.

has been observed experimentally, is described in section 5. The transformation to the adsorbed formate anion from molecularly adsorbed *cis-* and *trans-*formic acid is described in sections 6 and 7, respectively. We examined the effect of electron correlations on these surface reactions at the MP2 level, and the results are described in section 8. Finally, the dynamic vibrational mode,[23,35] which seems to be involved in the decomposition reaction of adsorbed formic acid, is described in section 9.

2. Model and Calculation Method

ZnO has a wurtzite crystal structure, as shown in Figure 2. For this study, we used the Zn$_4$O$_4$ cluster shown in Figure 3, embedded in an electrostatic field that simulates the Madelung potential. The Zn$_4$O$_4$ cluster includes the first, second, and third layers. The cluster is small, and it includes only two of the three nearest neighbors of the reaction sites. Thus, the cluster is more reactive than the actual surface, and our results may overestimate the reactivity. However, we believe that our results are correct qualitatively. In our previous paper,[24] we examined the effect of the electrostatic field on the dissociative adsorption of a hydrogen molecule on ZnO(10$\bar{1}$0). The Madelung potential is proportional to the ionic charge, q, in Zn$^{+q}_4$O$^{-q}_4$. Mulliken's atomic charge for the Zn$_4$O$_4$ cluster calculated at the Hartree−Fock level is about ±1.0. However, the electron density is spread over the atomic region so that we have to use smaller point charges to simulate the Madelung potential. The first and second layers of the ZnO crystal shown in Figure 2 are expressed by Zn$_{60}$O$_{60}$ and the third and fourth layers by Zn$_{56}$O$_{56}$. The complete ZnO model used in this study has eight layers (four sheets). The Zn$_4$O$_4$ cluster is located at the center of the surface, and we placed the point charges, +0.5 on Zn and −0.5 on O, at the 464 lattice sites around the Zn$_4$O$_4$ cluster.

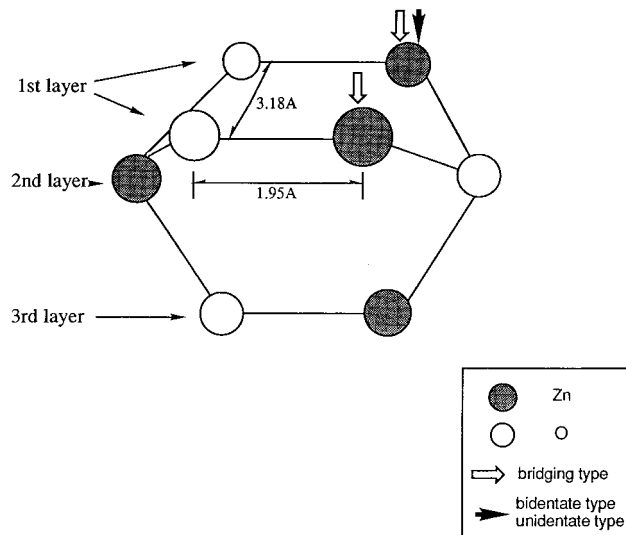The cluster geometry is fixed in the crystal lattice position with a Zn−O distance of 1.95 Å during surface reaction

processes. A surface relaxation effect might be important in the chemisorption and surface reaction processes. However, since the surface has a large number of degrees of freedom, a formidably large calculation is necessary if such effects are included in the reaction path calculations. Therefore, in the present study, we did not include the effect of the relaxation of the ZnO surface. Only the geometries of the adsorbates were optimized using the energy gradient method.

For the reaction site for the adsorption and dissociation of formic acid, we used the Zn$_2$O$_2$ portion of the cluster of the first layer. For example, the bridging and bidentate formic acids are assumed to be adsorbed on the Zn atoms shown by the arrows in Figure 3. The molecular plane of the adsorbed formate species on the metal and metal oxide surfaces has been reported to be perpendicular to the surface.[10,23,36] Therefore, the molecular plane of molecularly and dissociatively adsorbed formic acid was assumed to be perpendicular to the surface, except when otherwise noted.

The basis set used for the Zn atom was the (3s2p5d)/[2s2p2d] set of Hay and Wadt, and the Ar core was replaced by an effective core potential.[37] For C and O atoms, the (9s5p)/[4s2p] sets of Huzinaga and Dunning were used,[38,39] while the (4s)/[2p] set was used for the H atom.

The Hartree−Fock and MP2 calculations were carried out using the HONDO7 program library.[40]

3. Adsorption of *cis*-Formic Acid

Formic acid is dissociatively adsorbed on the ZnO surface at room temperature[3] and is molecularly adsorbed on various metal surfaces.[20,22] However, the molecular adsorption of formic acid on the ZnO(10$\bar{1}$0) surface has never been reported. Therefore, we first investigated the molecular adsorption of formic acid on the ZnO(10$\bar{1}$0) surface.

We assume there are three typical structures for molecularly adsorbed *cis*-formic acid, bridging, bidentate and unidentate, as shown in Figure 1. We tried to find stable structures that could be assigned to these three structures. The plane of formic acid is kept perpendicular to the ZnO surface to optimize the structure. Two optimized geometries of the adsorbed species are shown in Figure 4.
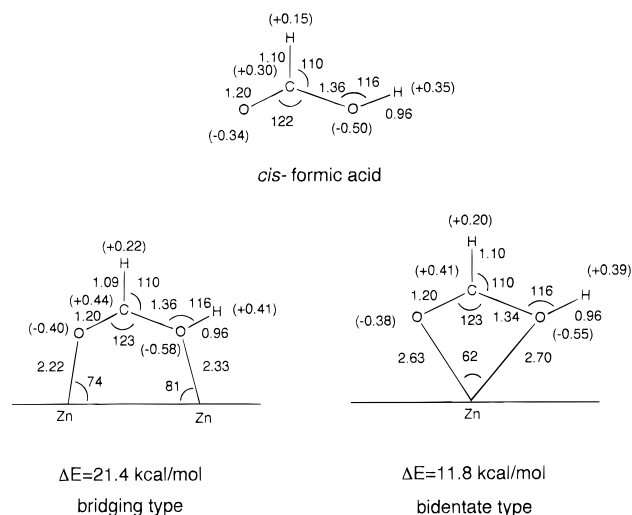
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cis- formic acid

ΔE=21.4 kcal/mol

bridging type

ΔE=11.8 kcal/mol

bidentate type

Figure 4. Fully optimized geometric parameters of free *cis*-HCOOH and *cis*-HCOOH adsorbed on a ZnO surface. Bond distances and angles are in angstroms and degrees, respectively. Values in parentheses show net atomic charges. The lack of symmetry for the bidentate structure reflects the lack of symmetry in the adsorption site shown in Figure 3.

Two O atoms of the formic acid interact with two surface Zn atoms in the bridging structure, and they interact with one surface Zn atom in the bidentate structure. The Zn−O distance in the bridging structure is 0.4 Å shorter than that in the bidentate structure, suggesting that the former is more stable than the latter. The internal geometry of formic acid is essentially the same in both structures and is little different from that of free *cis*-formic acid.

We calculated the adsorption energy as

$$\Delta E = E(\text{molecular adsorption}) - E(\text{Zn}_4\text{O}_4) - E(cis\text{-formic acid}) \quad (1)$$

The adsorption energies of the bridging and bidentate structures are −21.4 and −11.8 kcal/mol, respectively. A stable structure that could be assigned to the unidentate structure was not found in our model calculations.

4. Adsorption of *trans*−Formic Acid

We next examined the adsorption of *trans*-formic acid on the ZnO(10$\bar{1}$0) surface. Three structures of the interaction between *trans*-formic acid and the ZnO(10$\bar{1}$0) surface were considered, as shown in Figure 5. In each structure, the O and H atoms of the formic acid interact with the surface Zn and O atoms, respectively. The *R* values denoted in Figure 5 are optimized under the following conditions. The geometry of formic acid is the same as that in the gas phase. The molecular plane of formic acid is assumed to be perpendicular to the surface, and the O−H axes, which are expressed by the broken lines in Figure 5, are assumed to be parallel to the Zn−O bond.

The adsorption energy was defined as

$$\Delta E = E(\text{molecular adsorption}) - E(\text{Zn}_4\text{O}_4) - E(trans\text{-formic acid}) \quad (2)$$

Table 1 shows the adsorption energy calculated at the optimized *R* values. The adsorption energy of *trans*-formic acid in Figure 5a is greater than that of *cis*-formic acid. This result shows that the H atom of formic acid interacts strongly with the surface O atom. The distance between nonbonded O and H atoms of formic acid and the Zn−O lattice distance are 2.43 and 1.95 Å, respectively, as shown in Figure 5a, while the Zn−O distance
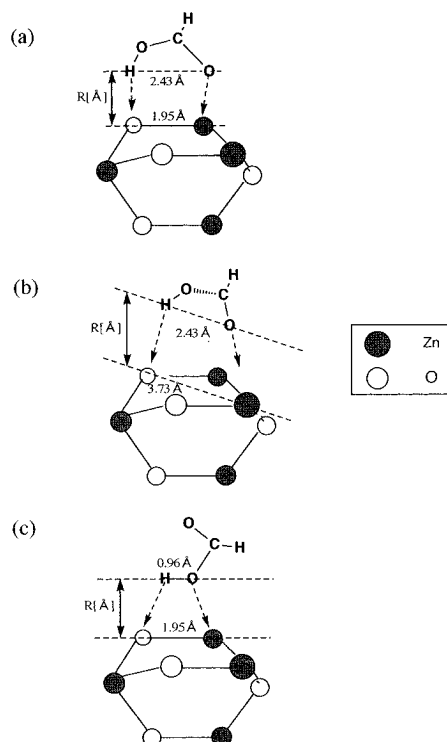

Figure 5. Assumed path for the molecular adsorption of *trans*-formic acid. *R* is the distance between formic acid and the surface.

TABLE 1: Distance between *trans*-Formic Acid and the ZnO Surface, *R* [Å], and the Adsorption Energy of *trans*-Formic Acid on the ZnO(10$\bar{1}$0) Surface, ΔE [kcal/mol]

structure[a]	*R*	ΔE[b]
a	2.0	−37.1 (−79.6)[c]
b	2.0	−22.1
c	2.2	−17.1

[a] The structure is shown in Figure 5. [b] The adsorption energy is defined by eq 2. [c] The adsorption energy for the optimized geometry.

trans- formic acid
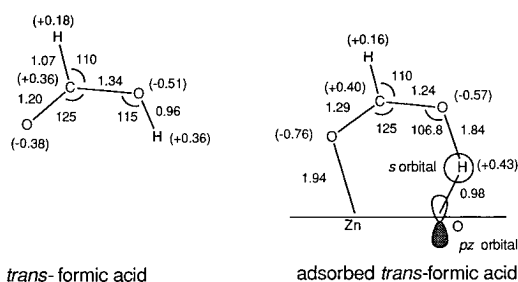
adsorbed *trans*-formic acid

Figure 6. Fully optimized geometric parameters of free *trans*-HCOOH and *trans*-HCOOH adsorbed on a ZnO surface. Bond distances and angles are in angstroms and degrees, respectively. Values in parentheses show the net atomic charges.

in Figure 5b is 3.73 Å. This makes the interaction in Figure 5a preferable to that in Figure 5b. In Figure 5c, the O−H distance is much smaller than the Zn−O distance, and the adsorption energy becomes smaller.

The geometric parameters of the formic acid in Figure 5a were optimized, and the result is shown in Figure 6. The adsorption energy is calculated to be −79.6 kcal/mol. The O−H bond is twice as long as that in the gas phase. The CO distance on the right side of HCOO becomes 1.24 Å, which is close to the single-bond length of C−O. The distance between H and surface O atoms is 0.98 Å, which is close to the standard O−H bond length. This result indicates that the O−H bond of formic acid should dissociate spontaneously with the formation of a surface OH species, while the adsorbed formate species
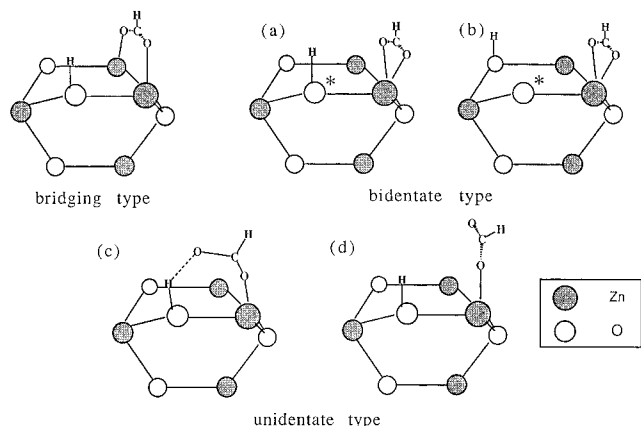
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Figure 7. Structures from the dissociative adsorption of formic acid that include the bridging structure, the bidentate structure (a and b), and the unidentate structure (c and d): (a) H⁺ adsorbed on the surface O atom located on the same side as the surface formate anion; (b) H⁺ is adsorbed on the surface O atom located on the side opposite the surface formate anion; (c) the surface formate anion interacts with the surface OH species; (d) only one O atom of the formate anion interacts with the surface Zn atom.

Figure 8. Optimized geometric parameters of free HCOO⁻ and HCOO⁻ adsorbed on a ZnO surface. Bond distances and angles are in angstroms and degrees, respectively. Values in parentheses are the net atomic charges.

continues to interact with the surface OH species, as seen from Figure 6. In the dissociation process of the proton, the $2p_z$ orbital of the surface oxygen donates an electron to the next LUMO of formic acid, which has an O—H antibonding character. Therefore, the O—H bond of formic acid is weakened and the surface OH species is formed.

When *cis*-formic acid approaches the ZnO surface, molecular adsorption and conversion among the molecularly adsorbed forms of formic acid occur on the ZnO surface. On the other hand, *trans*-formic acid is dissociatively adsorbed to form surface formate and OH species with no energy barrier. We will discuss in detail these adsorbed *trans*-formic acids.

The dissociation of the proton from the *trans*-formic acid on the ZnO surface occurs with no energy barrier, while more than 17 kcal/mol is necessary to dissociate the proton from the *trans*-formic acid on the MgO surface.[34] Thus, the dissociation of a proton from adsorbed organic compounds on a ZnO surface is expected to be more favorable than from those on a MgO surface.

5. Adsorption Geometry of Formate Anion

We next examined the stable adsorption geometry and the adsorption energy of the formate anion generated on the ZnO-(1010) surface. As candidates for stable geometries, we examined the bridging, bidentate, and unidentate structures shown in Figure 1. In the bridging and bidentate formates, two oxygen atoms interact with lattice Zn atom(s), while only one oxygen atom interacts with a lattice Zn atom in the unidentate formate. The molecular plane of HCOO is assumed to be perpendicular to the ZnO plane and stands on the Zn atoms. Figure 7 shows the structures for the formate anion and the surface OH that are assumed to be possible and that are used as initial guesses to optimize the geometries. The unidentate structure in Figure 7d is unstable. On the other hand, the unidentate structure in Figure 7c, which is the same as that shown in Figure 6, is stable since HCOO can interact with the surface OH species.

The optimized geometries for the bridging and bidentate structures are shown in Figure 8 together with that of the free formate anion in the gas phase. The values in parentheses are the Mulliken gross charges. The geometries of the bridging and bidentate structures are almost the same as that of the free
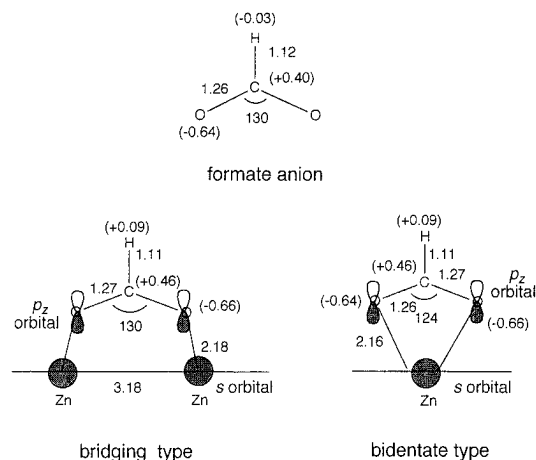
formate anion. The OCO angle in the bidentate structure is less than that in the bridging structure or the free anion. Both the bridging and bidentate structures are stabilized by the overlap between the unoccupied s orbital of the Zn atom and the occupied $2p_z$ orbital of the O atom of the formate anion, as shown in Figure 8. Each $2p_z$ orbital of the O atom of the formate anion interacts with each s orbital of the Zn atom in the bridging structure, while the two p_z orbitals of the O atoms of the formate anion interact with only one s orbital of the Zn atom in the bidentate structure. The OCO angle in the bidentate structure decreases to achieve a greater overlap of these orbitals. This strain in the OCO angle makes the bidentate structure unstable. Note that the HCOO geometry of the unidentate structure shown in Figure 6 is close to that of the free formate anion shown in Figure 8.

The $2p_z$ orbitals of the two oxygen atoms in the first layer constitute the HOMO before the formate anion is adsorbed on the Zn atom. After it is adsorbed on the Zn atom, one of the $2p_z$ orbitals, marked by an asterisk in Figure 7, becomes the HOMO and the other one decreases in energy. Thus, the nearest neighbor oxygen of the formate anion is activated. The difference in the stability of bidentate structures a and b is caused by this surface activation. Similar surface activations with the adsorption of the formate anion were also observed for the MgO-(001) surface.[34]

The total charges of HCOO⁻ are −1.0, −0.77, −0.75, and −0.77 for the free, bridging bidentate a and unidentate c structures, respectively. Some electron transfer occurs from the formate anion to the surface. The charge on the hydrogen atom of the surface OH species is +0.37. The total charge of the adsorbed HCOO and H atoms is about −0.4, and this is the amount of electron transfer from the surface to the dissociated species.

On the ZnO surface, the bridging structure and unidentate structure c are calculated to be more stable than the bidentate structure: the heats of adsorption, ΔE, are calculated to be −79.8 and −79.6 kcal/mol for the bridging and unidentate structures, respectively, as shown in Table 2:

$$\Delta E = E(\text{dissociative adsorption}) - E(\text{Zn}_4\text{O}_4) -$$
$$E(\text{\textit{trans}-formic acid}) \quad (3)$$

Noto *et al.*[3] suggested that the formate anion assumes a bridging or bidentate structure on the ZnO surface based on an IR experiment. Petrie and Vohs[5] reported that formic acid is

TABLE 2: Distance between the Adsorbed Formate Anion and the ZnO Surface, R [Å], and the Adsorption Energy of the Adsorbed Formate Anion on the ZnO(10$\bar{1}$0) Surface, ΔE [kcal/mol]

structure[a]	R	ΔE[c]
bridging[a]	2.15	−79.8
bidentate a	1.86	−56.4
b	1.92	−28.5
unidentate c[b]	1.92	−79.6

[a] The structure is shown in Figure 7. [b] The structure is shown in Figure 7. The optimized geometrical parameters are shown in Figure 6. [c] The adsorption energy is calculated using eq 2. a
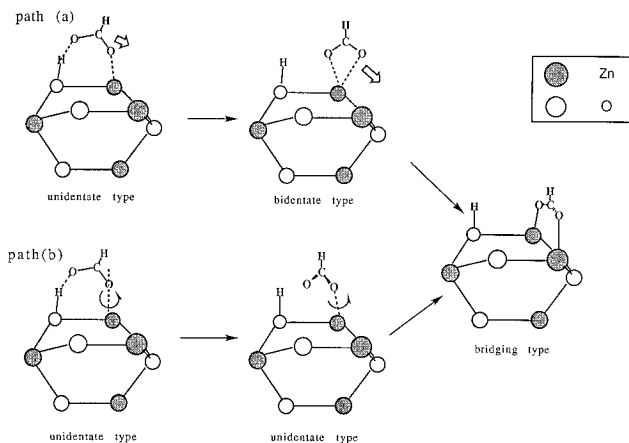

Figure 9. Transformation paths of the formate anion on a ZnO surface from the unidentate structure to the bridging structure. In path a, the bidentate structure is formed in the process of forming the bridging structure.

Figure 10. Energy profiles for transformation paths a and b in Figure 9 from the unidentate structure to the bridging structure of the formate anion on a ZnO surface.

molecularly adsorbed on the (0001)-Zn surface of ZnO at a low temperature of only 160 K: it exhibits hydrogen bonding with the surface, and intramolecular hydrogen bonding exists among adsorbates. When heated to 400 K, formic acid dissociates into a unidentate formate anion. Interaction between the adsorbed formate anion and the surface has not been observed on a nonpolar ZnO(10$\bar{1}$0) surface. These experiments also suggested that molecularly adsorbed formic acid exists on the ZnO surface. Our present results suggest that both the unidentate and bridging structures exist on the ZnO(10$\bar{1}$0) surface.

6. O−H Bond Cleavage from the Unidentate (Trans) Form

We next examined possible routes and mechanisms for the conversion of the unidentate structure to the bridging structure. We assumed two paths, as shown in Figure 9. The initial structure has been discussed in Sections 4 and 5. The geometry of the formate anion and the distance between H and the surface O atoms are fixed during the transformation. In path a, the formate anion moves toward the neighboring Zn atom to form a bidentate structure, which is eventually transformed into the bridging structure. In path b, only one O atom of the formate anion continues to interact with the surface Zn atom, and the formate anion is rotated around this Zn−O axis to give the bridging structure. The unidentate formate anion is formed during the transformation in path b. The energy profiles for these two paths are shown in Figure 10. The unidentate structure is not stable if it does not interact with the surface OH species, as shown in Figure 7c. Therefore, path a is more favorable than path b, and the energy barrier is around 15 kcal/mol. Since the movements in these paths are considerably constrained, this barrier would be an upper bound.
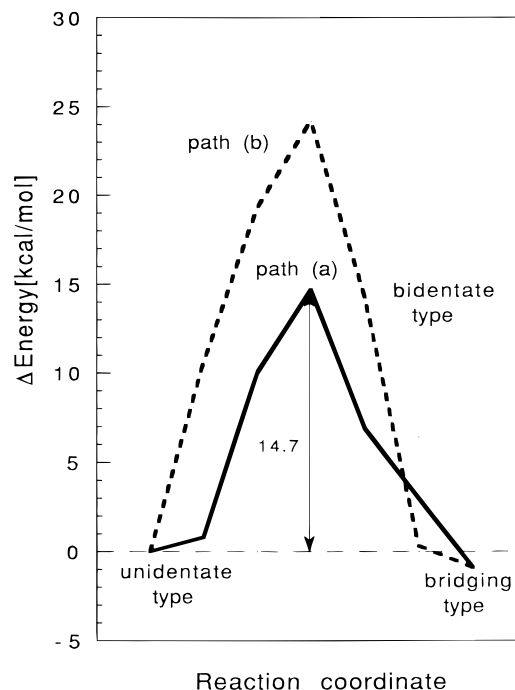
7. O−H bond Cleavage from Adsorbed *cis*-Formic Acid

We next examined possible routes and mechanisms for transformation from the molecular to the dissociative adsorption of formic acid on a ZnO(10$\bar{1}$0) surface. Here, we consider the routes starting from *cis*-formic acid adsorbed on the surface.

Figure 11 shows the assumed pathway of the O−H bond cleavage of molecularly adsorbed *cis*-formic acid. We choose the bridging structure, which is the most stable structure (Figure 4) for molecularly adsorbed *cis*-formic acid. The migration path of the H atom is optimized, while the geometry of the formate anion is fixed during optimization. An overview of the path is shown in Figure 11a, and the yz and xy planes are shown in parts b and c of Figure 11, respectively. The O−H bond distance and the distance between H and the surface O atoms are given in Figure 11b. Areas indicated by #0 and #4 are the structures of the molecular and dissociative adsorptions, respectively. The O−H bond is retained during the move from #0 and #1. O−H bond cleavage starts at #2, and the surface O−H bond is formed around #3. The energy barrier is 11.7 kcal/mol at #2, as shown in Figure 12. The dissociative adsorption of formic acid on a ZnO surface at room temperature has been reported.[3] The value of 11.7 kcal/mol is a reasonable energy barrier for this reaction at room temperature. Therefore, we think that this reaction is possible at room temperature.

8. Effect of Electron Correlation

We examined the effect of electron correlations on adsorption and conversion among the dissociatively adsorbed formate species at the MP2 level. The results are shown in Table 3. We used geometries that had been optimized at the HF level. The energy barriers of both reactions are almost the same as those at the HF level. The use of electron correlations at the MP2 level does not change the qualitative nature of the surface reaction on the ZnO surface.

9. Tilting of the Formate Anion Toward the Surface

A dynamic bending mode of the adsorbed formate anion, in which it is tilted toward the surface, has been observed on an Ag surface.[23]
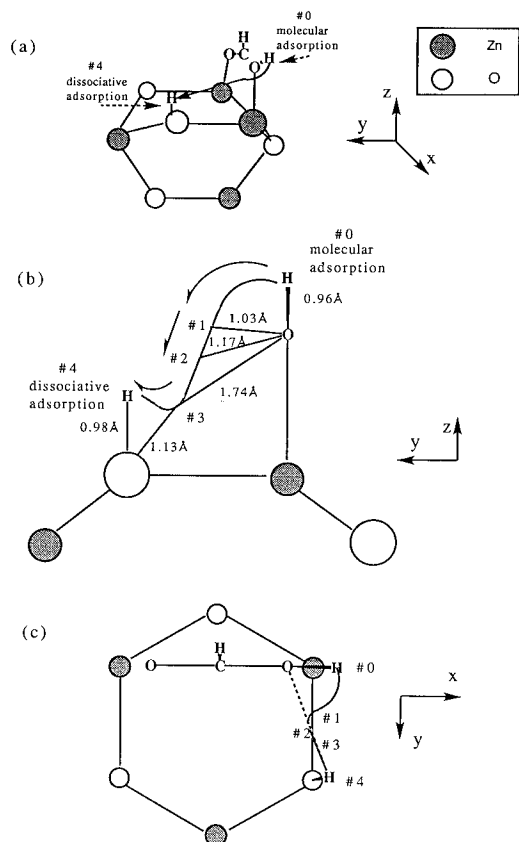
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Figure 11. Dissociation path of the OH bond of molecularly adsorbed *cis*-HCOOH on a ZnO surface: (a) an overall view; (b) view of the *yz* plane; (c) view of the *xy* plane. The characters #1 and #4 denote the geometries of the molecular and dissociative adsorptions, respectively.
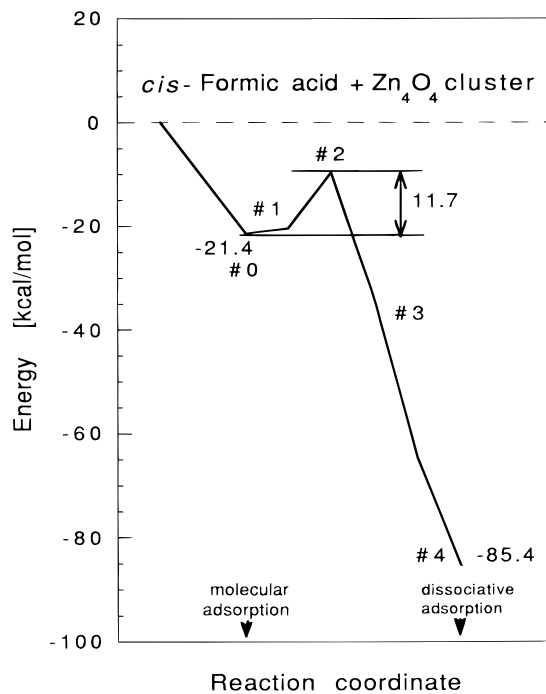
Figure 12. Dissociation path of the OH bond of molecularly adsorbed *cis*-HCOOH on a ZnO surface.

During the decomposition of formic acid into $CO + H_2O$ or $CO_2 + H_2$ on the surface, cleavage of the C–O and/or C–H bond should be the rate-determining step. Since the C–H bond interacts more effectively with the surface if the formate anion is tilted toward the molecular plane, we expect that this mode is important for inducing cleavage of the C–H bond.

TABLE 3: Effect of Electron Correlation on the Energy Barrier of the Dissociative Adsorption of *cis*-Formic Acid and *trans*-Formic Acid

	energy barrier	
	HF	MP2
cis-HCOOH$_{(g)} \rightarrow$ HCOO$_{(a)}$ + OH$_{(a)}$[a]	11.7	7.5
$trans$-HCOOH$_{(g)} \rightarrow$ HCOO$_{(a)}$ + OH$_{(a)}$[b]	14.7	18.4

[a] The energy barrier for the dissociative adsorption of *cis*-formic acid to form bridging HCOO and the surface OH species on the ZnO surface. [b] The energy barrier for the dissociative adsorption of *trans*-formic acid to form bridging HCOO and the surface OH species on the ZnO surface.
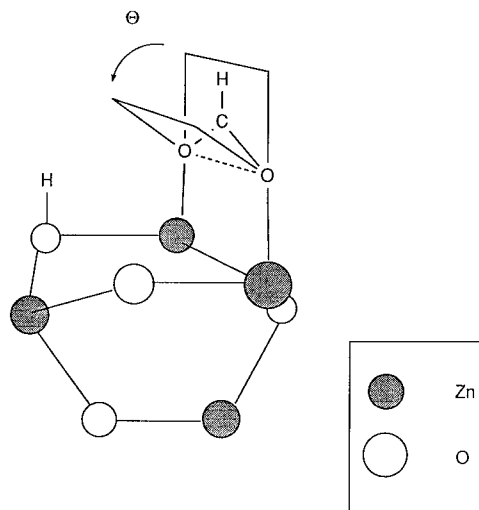
Figure 13. Tilting of the formic anion toward the ZnO(10$\bar{1}$0) surface. $\Theta = 0$ denotes that the molecular plane is vertical to the surface, and $\Theta = 90$ denotes that the molecular plane is parallel to the surface.
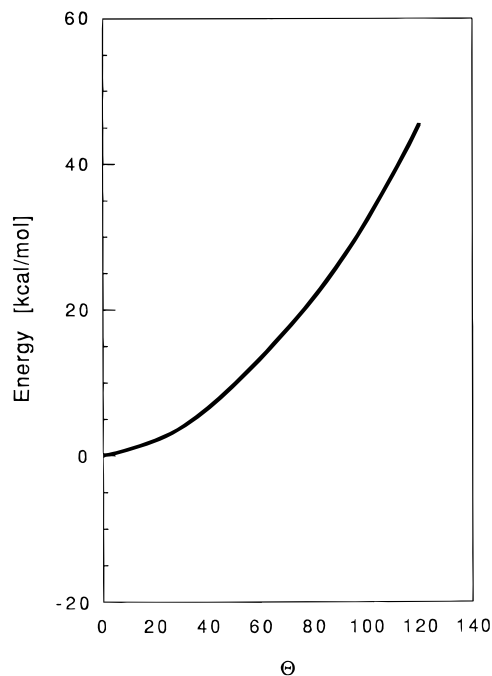
Figure 14. Potential curve for tilting of the adsorbed formate anion toward the ZnO(10$\bar{1}$0) surface.

We examined whether the molecular plane of the formate ion tilts toward the ZnO(10$\bar{1}$0) surface and, if so, how much and how easily it tilts. Figure 13 shows tilting of the formate molecular plane toward the ZnO surface. We used the bridging geometry and fixed both the height of the two oxygen atoms of the adsorbed formate anion above the surface and the geometry of the formate. Although relaxation of the formate anion is

not considered, we believe that the qualitative significance of our results is not affected. In this figure, Θ denotes the angle between the molecular plane and the plane vertical to the surface. $\Theta = 0$ means that the formate ion is vertical to the surface and $\Theta = 90$ means that it is parallel to the surface.

The potential curve is shown in Figure 14. The oxygens of the formate anion have lone-pair orbitals both in-plane and out-of-plane, and therefore, the out-of-plane orbital can interact with a Zn atom when the formate anion tilts toward the surface. In addition, there is no steric hindrance for the tilting of this molecule on the ZnO(10$\bar{1}$0) surface, as shown in Figure 2. These two points result in a very small tilting energy. On the MgO-(001) surface, the most stable structure occurred at $\Theta = 30$, which was more stable than $\Theta = 0$ by 4 kcal/mol.

We are currently investigating the mechanism of the decomposition of formic acid on metal oxide surfaces.

10. Summary

We performed a theoretical investigation of the reaction route and the mechanism of the molecular and dissociative adsorption of formic acid on a ZnO(10$\bar{1}$0) surface by means of the *ab initio* molecular orbital method. As a model of the surface, we used Zn_4O_4 embedded in an electrostatic field represented by 464 point charges at the lattice positions of the crystal. The results can be summarized as follows.

Experimental studies have suggested that $HCOO^-$ exists in a bridging or bidentate structure on the ZnO(10$\bar{1}$0) surface.[3] However, the energy difference between the bridging structure and the unidentate structure in interactions with the surface OH species was calculated to be very small in this study. Thus, we believe that both the bridging and unidentate structures are favorable and the bidentate structure is unfavorable.

cis-Formic acid is molecularly adsorbed without an energy barrier and is stabilized on the surface by 21.4 kcal/mol. The OH bond of the formic acid then cleaves to form an adsorbed formate anion and a proton. This proton is associated with the surface oxygen. The energy barrier for this process is 11.7 kcal/mol.

On the other hand, *trans*-formic acid is dissociatively adsorbed without an energy barrier and is stabilized on the surface by 79.6 kcal/mol. In this case, the formate anion interacts with the surface OH species.

We found that the p orbital of the surface O atom adjacent to the adsorption site of the formate anion is activated by the presence of the adsorbed bidentate formate anion. This activation could affect the paths and barriers of reactions occurring on this surface.

The formate anion easily tilts toward the surface, which leads to greater interaction between the formate anion and the surface.

Finally, we should comment on the reaction paths and the energy barriers described here. Since there are a large number of degrees of freedom for the surface reaction, we tried to determine the prospective reaction paths based on our experience and after many preliminary investigations. Although it is impossible to examine every possibility, we believe that the reaction paths presented in this paper are quite reasonable. Furthermore, our calculations using these reaction paths give an upper bound for the barrier since the constraints on the stable geometries are less than those on the transition states. Thus, although our analysis was essentially qualitative, we believe that the reaction mechanisms and reaction paths described here are valid.

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