

Cluster quantum-chemical MINDO/3 study of HCOOH interactions with nonpolar (10 $\bar{1}0$) surface of ZnO

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Abstract

A modified MINDO/3 method was applied to the study of formic acid interactions with a nonpolar (10 $\bar{1}0$) surface of pure zinc oxide. Molecular adsorption of both *cis*- and *trans*-HCOOH takes place on coordinatively unsaturated active sites including two-coordinated zinc cations, i.e., Zn_{2C}²⁺ centres. Regular (10 $\bar{1}0$) surface of ZnO containing three-coordinated both acid and base centres are inactive at low or room temperatures; they are activated under relatively moderate temperature regions. Dissociative adsorption of HCOOH leads to the formation of a formate anion stabilized on an acid sites and of a proton connected to a basic site. For a formate anion fragment, a bridge or a bidentate structure is energetically more preferable compared to an unidentate structure. On the basis of the computational results, two channels of dissociative adsorption of HCOOH are discussed.

Keywords: HCOOH; Zinc oxide; Quantum-chemical study

1. Introduction

Chemical activity of metal oxides in the catalytic processes could be described by the existence of low-coordinated acid–base pair of centres in various structural defects of an oxide surface, i.e., steps, edges, corners, kinks, etc. [1–6]. This is also the case for ZnO, which is an n-type semiconductor of wurtzite type structure and has a catalytic activity in olefin hydrogenation, CO oxidation, synthesis-gas conversion to methanol and higher branched or linear alcohols, etc. [7–12]. It is also known that the

decomposition of methanol, formaldehyde and formic acid easily takes place on ZnO catalysts [13,14].

Several theoretical studies have been performed for the adsorption of small molecules on pure zinc oxide surfaces, in particular for the adsorption of H₂, CO, methane, O₂, etc. (see, for example [4,5,15,16] and references therein). However, to our knowledge no detailed theoretical studies have been performed on the interaction of formic acid on zinc oxide surface.

In the present paper, results are reported on cluster quantum-chemical calculations by a modified MINDO/3 method for the interaction of formic acid with nonpolar (10 $\bar{1}0$) surface of zinc oxide. Based on these calculational results,

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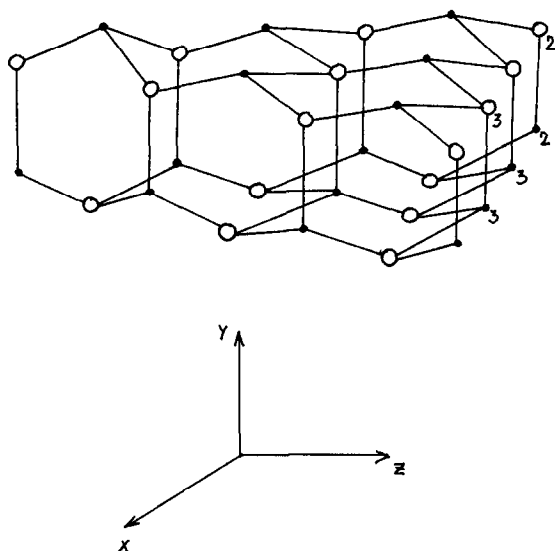


Fig. 1. $Zn_{16}O_{16}$ molecular cluster used as a model of nonpolar $(10\bar{1}0)$ surface of zinc oxide. Numbers correspond to the degree of coordination (LC) of cations and anions. Symbols: \bullet Zn_{LC}^{2+} , \circ O_{LC}^{2-} .

two channels of dissociative adsorption and the nature of molecular adsorption of formic acids are discussed.

2. Method of calculation and surface model

Cluster quantum-chemical calculations were performed within the framework of the MINDO/3 method; its parameterization extended for studying Zn-containing compounds [4]. Nonpolar $(10\bar{1}0)$ surface of zinc oxide were modelled by the same four-layer molecular cluster of $Zn_{16}O_{16}$ (Fig. 1), as described elsewhere [4,5]. It should be noted that the latter cluster model allows us to analyse the participation of low-coordinated acid–base centres (Zn_{LC}^{2+} and O_{LC}^{2-} ions) in the adsorptive interaction. Total optimization of geometry of both the initial cluster and a formic acid were carried out. For all adsorption complexes presented here the internal coordinates of the adsorbate molecules were fully optimized, whereas only the active site(s) coordinates of zinc oxide cluster were allowed to relax. Some additional calculations

were performed to clarify the effects of next-neighbour pair of a two-coordinated acid and base centres on energetics of molecular and dissociative adsorption of HCOOH using relatively small Zn_4O_4 cluster model. Moreover, the influence of the cluster size on the energetics of dissociative adsorption of HCOOH were examined via using the similar four-layer molecular clusters of Zn_nO_n , where $n = 4, 9, 16, 25, 36, 49$. In the latter two cases, the geometry of Zn_nO_n cluster models were fixed at the values corresponding to the experimental bulk structure of ZnO.

3. Interaction of HCOOH with nonpolar $(10\bar{1}0)$ surface of ZnO

3.1. Molecular adsorption

Formic acid has two structural isomers, *cis*- and *trans*-HCOOH. According to MINDO/3 calculations and in agreement with available theoretical investigations [16], *trans*-HCOOH is relatively more stable than *cis*-HCOOH. Since the energy difference for these two forms are relatively small (3.4 and 6.4 kcal/mol with MINDO/3 and ab initio [16] methods, respectively), we can suggest that they exist as a mixture of these two forms in the gas phase.

First of all, we consider the molecular adsorption of *cis*-HCOOH. In the theoretical point

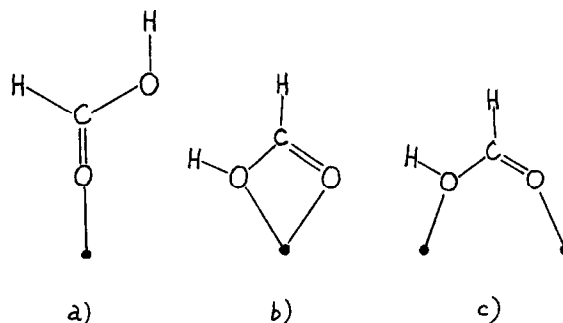


Fig. 2. Molecular adsorption of *cis*-HCOOH on nonpolar $(10\bar{1}0)$ surface of zinc oxide forming (a) an unidentate, (b) a bidentate and (c) a bridge structures. Symbols: \bullet Zn_{LC}^{2+} , \circ O_{LC}^{2-} .

Table 1

Optimized geometries (bond lengths in Å, angles in degrees) and heats of molecular adsorption (ΔE , kcal/mol) of *cis*-HCOOH on nonpolar (10 $\bar{1}$ 0) surface of zinc oxide as calculated by the MINDO/3 method

Active site	Type of complex	Geometry ^a	E^b
Zn _{3C} ²⁺	Bidentate	ZnO, 3.118 (3.428); CO, 1.207 (1.321); OCO, 126; OH, 0.950; HOC, 117; CH, 1.140	–8.7
Zn _{2C} ²⁺ –Zn _{3C} ²⁺	Bridge	ZnO, 2.732 (2.902); CO, 1.208 (1.326); OCO, 127; OH, 0.951; HOC, 116; CH, 1.140	–3.8
Zn _{3C} ²⁺	Unidentate	ZnO, 2.651; CO, 1.209 (1.319); OCO, 127; OH, 0.949; HOC, 116; CH, 1.141	–3.0
Zn _{2C} ²⁺ ^c	Unidentate	ZnO, 2.390; CO, 1.209 (1.316); OCO, 127; OH, 0.950; HOC, 116; CH, 1.140	5.1
Zn _{2C} ²⁺ ^d	Unidentate	ZnO, 2.593; CO, 1.330 (1.203); OCO, 126; OH, 0.951; HOC, 118; CH, 1.141	–3.0
Zn _{2C} ²⁺	Bidentate	ZnO, 2.608 (2.854); CO, 1.210 (1.326); OCO, 126; OH, 0.950; HOC, 118; CH, 1.138	4.0
Free	<i>cis</i> -HCOOH ^e	CO, 1.202 (1.321); OCO, 128; HOC, 116; OH, 0.948; CH, 1.143	

^a Second type of a bond length including O atom of C–O group of *cis*-HCOOH are given in parenthesis.

^b (+) Sign means that the products are lower in energy than the reagents.

^c Adsorption via O atom of the C=O group.

^d Adsorption via O atom of C–O group.

^e Gas phase *cis*-HCOOH.

of view there are three possibilities for adsorption of *cis*-HCOOH and they correspond to the formation of a bridge, a bidentate and an unidentate structures (Fig. 2). In a bridging structure, each O atom of *cis*-HCOOH interacts with a next-neighbour surface Zn atom, while in a bidentate structure each O atom of *cis*-HCOOH is coordinated to one and the same surface Zn atom and, finally, in an unidentate structure O atom of the C=O group of *cis*-HCOOH directly coordinates to surface Zn atom (Fig. 2). Therefore, the adsorption mechanism to be expected is very simple and correspond to the interaction of a lone electron pair of the O atom(s) of *cis*-HCOOH and a vacant orbital of surface acid site(s), i.e., Zn_{LC}²⁺ cation(s).

Table 1 shows optimized geometry characteristics and adsorption energies of these adsorption complexes. The latter is calculated as an energy difference between the adsorption complex and the sum of the initial free cluster and *cis*-HCOOH. It is clear that molecular adsorption of *cis*-HCOOH takes place only on a coordinatively unsaturated Zn_{2C}²⁺ acid sites. However, adsorption energy is very small and correspond to a very weak interaction due to very large Zn–O bond length between the surface Zn atom and O atom of adsorbed *cis*-HCOOH. Regular (10 $\bar{1}$ 0) surface of ZnO containing a three-coordinated Zn_{3C}²⁺ sites is inactive for the

molecular adsorption of *cis*-HCOOH. Perhaps, these centres will be activated under relatively moderate temperatures. This is due to an energy consumptions necessary for a relaxation of active sites interacting with adsorbed particles. This question will be dealt with in detail later when we will consider the dissociative adsorption of HCOOH.

The formation of an unidentate structure is more favourable than of a bridge or a bidentate structures. However, the gain in energy due to the adsorptive interaction of *cis*-HCOOH on three-coordinated acid site(s) is not enough to cover an energy consumption for a relaxation of Zn_{3C}²⁺ sites. In all cases a little charge transfer (less than 0.15 e) from adsorbed *cis*-HCOOH to the surface takes place. The geometry of adsorbed *cis*-HCOOH is almost the same as that of free *cis*-HCOOH.

Let us consider the molecular adsorption of *trans*-HCOOH on the (10 $\bar{1}$ 0) surface of ZnO. There are also three theoretically possible structures, shown in Fig. 3. In the first two adsorption complexes, *trans*-HCOOH interacts with a next-neighbour pair of Zn_{LC}²⁺–O_{LC}²⁻ acid–base centres forming a six- and a four-membered structure, respectively, while in the third case a six-membered structure will be formed on the distant pair Zn_{LC}²⁺–O_{LC}²⁻ acid–base centre. Table 2 shows optimized geometry characteristics and

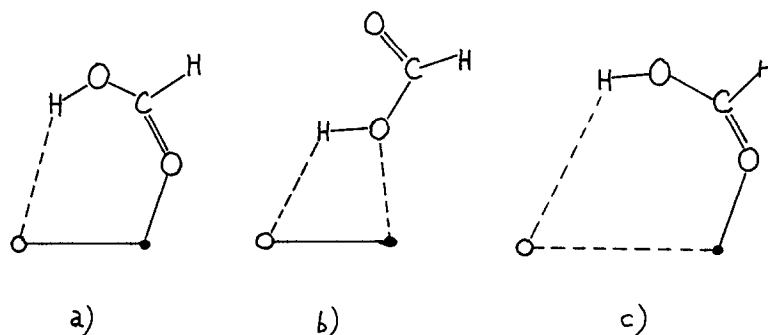


Fig. 3. Molecular adsorption of *trans*-HCOOH on the nonpolar (10 $\bar{1}0$) surface of zinc oxide forming (a) a six- and (b) a four-membered structures on a next-neighbour pair of acid–base centres and (c) a six-membered structure on a distant pair of acid–base centres. Symbols: ● Zn $_{2C}^{2+}$, ○ O $_{2C}^{2-}$.

adsorption energies for these structures. As in the case of *cis*-HCOOH, we found that (i) molecular adsorption proceeds only on a coordinatively unsaturated pair of Zn $_{2C}^{2+}$ –O $_{2C}^{2-}$ sites and its adsorption energy is slightly higher than that of *cis*-HCOOH. Inclusion of a H-bonding by using our modified version of MINDO/3-HB method [17,18] has only little effect: adsorption energy increases only for 0.9 kcal/mol due to the shortening of the H-bond between the H atom of *trans*-HCOOH and the surface O $_{2C}^{2-}$ site to 2.109 Å (Table 2); (ii) regular (10 $\bar{1}0$) surface of ZnO containing a three-coordinated

pair of acid–base centres is less active for molecular adsorption; (iii) geometry of an adsorbed *trans*-HCOOH do not practically change compared to free *trans*-HCOOH; (iv) relatively little charge transfer (less than 0.11 e) from an adsorbed HCOOH to the surface takes place.

3.2. Dissociative adsorption

Since the dissociated fragments of HCOOH do not depend on the precursor forms of HCOOH, we next examine the dissociative adsorption of *trans*-HCOOH. This dissociation of

Table 2

Optimized geometries (bond lengths in Å, angles in degrees) and heats of molecular adsorption (ΔE , kcal/mol) of *trans*-HCOOH on nonpolar (10 $\bar{1}0$) surface of zinc oxide as calculated by the MINDO/3 method

Active site	Geometry ^a	E^b
Zn $_{3C}^{2+}$ –O $_{3C}^{2-}$ ^c	ZnO, 2.659; CO, 1.209 (1.315); OCO, 135; OH, 0.954 (5.222); HOC, 119; CH, 1.139	–2.3
Zn $_{3C}^{2+}$ –O $_{3C}^{2-}$ ^d	ZnO, 2.808; CO, 1.210 (1.314); OCO, 135; OH, 0.953 (6.277); HOC, 119; CH, 1.138	–3.3
Zn $_{3C}^{2+}$ –O $_{3C}^{2-}$ ^e	ZnO, 8.946; CO, 1.204(1.319); OCO, 135; OH, 0.953 (8.161); HOC, 118; ZnOH, 65	no bond
Zn $_{2C}^{2+}$ –O $_{2C}^{2-}$ ^f	ZnO, 2.383; CO, 1.211 (1.311); OCO, 135; OH, 0.953 (4.653); HOC, 120; CH, 1.136	5.7
Zn $_{2C}^{2+}$ –O $_{2C}^{2-}$ ^g	ZnO, 2.424; OC, 1.206 (1.296); OCO, 136; OH, 0.978 (2.109); HOC, 110; CH, 1.100	6.6
<i>trans</i> -HCOOH ^h	CO, 1.204(1.320); OCO, 135; OH, 0.953; HOC, 118; CH, 1.137	

^a Second type of a bond length including O atom of C–O group of *trans*-HCOOH or H-bond length between H atom of *trans*-HCOOH and the surface O atom are given in parenthesis.

^b (+) Sign corresponds to stabilization of an adsorbed complex.

^c Next-neighbour acid–base pair centres.

^d Distant acid–base pair centres.

^e Same as ^c, but with the formation of four-membered structure.

^f Next-neighbour two-coordinated acid–base pair centres.

^g The same as ^f but as calculated by MINDO/3-HB method [17,18].

^h Gas phase *trans*-HCOOH.

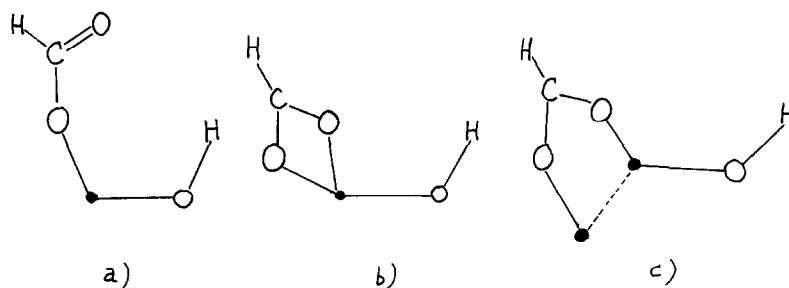
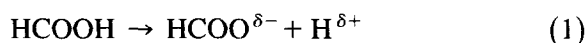


Fig. 4. Dissociative adsorption of *trans*-HCOOH on nonpolar (10 $\bar{1}0$) surface of zinc oxide forming a proton and formate anion with (a) an unidentate, (b) a bidentate and (c) a bridge structure. Symbols: ● Zn $_{2C}^{2+}$, ○ O $_{2C}^{2-}$.

trans-HCOOH correspond to the following scheme



and in the every structure a proton is connected to a basic sites, while a formate anion fragment can be adsorbed as an unidentate, a bidentate or a bridge structure (Fig. 4). Table 3 shows optimized geometry characteristics and adsorption energies for these structures. As evident, dissociative adsorption of *trans*-HCOOH proceeds on a coordinatively unsaturated pair of Zn $_{2C}^{2+}$ –O $_{2C}^{2-}$ acid–base centres with high efficiency. In contrast to molecular adsorption, for the dissociative adsorption of HCOOH the formation of a bridge structure is more energetically preferable than that of an unidentate or a bidentate structures on regular (10 $\bar{1}0$) surface of ZnO containing a three-coordinated pair of acid–base centres. The effective charge on the proton is

about 0.3 e, while on the formate anion fragment it is -0.5 e. On these structures, the geometry of the formate anion is strongly differs from that of free *trans*-HCOOH: the C–H bond length increases while the bond length between the C and O atoms of the formate anion becomes an average of the C–O and C=O bonds. It should be noted also that an effective relaxation of surface active sites takes place under dissociative adsorption, i.e., the active sites of interest are substantially moved from their optimal positions within the noninteracting cluster to the direction of an adsorbed fragments.

To clarify how much energy consumption takes place for these relaxation, we performed the following calculations. First, the geometry of a two-coordinated pair of Zn $_{2C}^{2+}$ –O $_{2C}^{2-}$ acid–base centres for the initial cluster is relaxed as that for dissociative adsorption of *trans*-

Table 3

Optimized geometries (bond lengths in Å, angles in degrees) and heats of dissociative adsorption (Å, kcal/mol) of *trans*-HCOOH on acid–base pair centres of nonpolar (10 $\bar{1}0$) surface of zinc oxide by scheme 1 as calculated by MINDO/3 method

Type of complex	LC ^a	Geometry ^b	E ^c
Unidentate	3	ZnO, 1.958; CO, 1.220 (1.288); OCO, 134; OH, 0.961; CH, 1.159	–12.0
Bidentate	3	ZnO, 2.327 (2.398); CO, 1.258 (1.267); OCO, 128; CH, 1.154; OH, 0.961	–18.9
Bridge	3	ZnO, 2.159 (2.173); CO, 1.260 (1.260); OCO, 133; CH, 1.154; OH, 0.959	2.9
Unidentate	2	ZnO, 1.923; CO, 1.221 (1.295); OCO, 133; CH, 1.155; OH, 0.953	23.0
Bidentate	2	ZnO, 2.234 (2.248); CO, 1.265 (1.268); OCO, 128; CH, 1.149; OH, 0.952	24.0

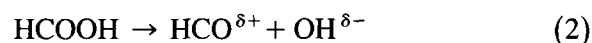
^a Coordination state of low-coordinated acid–base pairs centres.

^b Second type of a bond length including O atom of formate anion are given in parenthesis.

^c (+) Sign corresponds to stabilization of the dissociated fragments.

HCOOH forming an unidentate structure. In this case, O_{2C}^{2-} and Zn_{2C}^{2+} are moved 0.162 and 0.629 Å, respectively, and the distance between them increases 0.317 Å compared to an adsorbate-free non-interacting cluster. For this relaxed cluster, we found an energy consumption of 20.3 kcal/mol. This amount of energy is compensated by dissociative adsorption of *trans*-HCOOH forming an unidentate structure, i.e., bond energies of the formate anion with Zn_{2C}^{2+} and the proton with O_{2C}^{2-} is enough to cover energy consumptions for the relaxation of the active centres and for breaking the O–H bond in *trans*-HCOOH. Dissociative adsorption energy of *trans*-HCOOH result only in an energy of 7.7 kcal/mol on the same pair of active sites with a fixed unrelaxed geometry and forming the same unidentate formate anion: it is three times less than that for a relaxed cluster model. This finding is one more argument on the importance of taking into account the relaxation effects in the chemisorptive interactions.

Let us now consider dissociative adsorption of HCOOH on this nonpolar (1010) surface of ZnO by a different scheme



In this case, a hydroxyl anion is coordinated to an acid site while an aldehyde-like fragment is connected to a basic site (Fig. 5). We consider two types of acid–base pair centres in which they are either three- or two-coordinated. Table 4 shows optimized geometry characteristics and adsorption energies for these two structures. As can be expected, dissociative adsorption could take place only on a two-coordi-

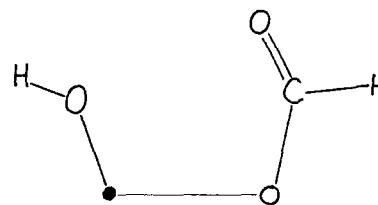


Fig. 5. Dissociative adsorption of *trans*-HCOOH on nonpolar (1010) surface of zinc oxide forming an aldehyde-like cation fragment and a hydroxyl anion. Symbols: ● Zn_{1C}^{2+} , ○ O_{1C}^{2-} .

nated acid–base pair centres. However, adsorption energy of this channel is much less than that for the formation of a formate anion and a proton. This means that the latter channel should be the main route of dissociative adsorption of HCOOH. Accordingly, this channel will lead to decomposition of formic acid on ZnO producing CO_2 and H_2 from precursor of an adsorbed formate anion and a proton, while the former one will lead to the formation of CO and H_2O .

Here, it is also interesting to estimate an energy barrier for HCOOH transformations by these pathways. Simple chemical intuition shows that for the reaction channel (2) the energy barrier should be higher than that for the reaction channel (1). We made an attempt to calculate these barriers within MINDO/3 method. In the latter case the HOZn angle formed between the OH-fragment of adsorbed HCOOH and the surface Zn–O bond is taken as reaction coordinate and the other geometry parameters were fully optimized. Note that this HOZn angle is equal to 127.6° and 68.2° for dissociative (Fig. 4a) and for molecular (Fig. 3a) adsorption of HCOOH on a next-neighbour pair of $Zn_{2C}^{2+}-O_{2C}^{2-}$

Table 4

Optimized geometries (bond length in Å, angles in degrees) and heats of dissociative adsorption (Å, kcal/mol) of *trans*-HCOOH on acid–base pair centres of nonpolar (1010) surface of zinc oxide by scheme 2 as calculated by MINDO/3 method

Type of complex	LC ^a	Geometry	E ^b
$Zn_{3C}^{2+}-O_{3C}^{2-}$	3	ZnO, 1.934; OH, 0.951; ZnOH, 125; O _s C ^c , 1.299; CO, 1.255; O _s CO, 125; CH, 1.146	–15.7
$Zn_{2C}^{2+}-O_{2C}^{2-}$	2	ZnO, 1.833; OH, 0.951; ZnOH, 118; O _s C ^c , 1.311; CO, 1.212; O _s CO, 132; CH, 1.162	9.7

^a Coordination state of next-neighbour acid–base pairs centres.

^b (+) Sign corresponds to stabilization of the dissociated fragments.

^c Superscript (s) relates to the surface O atom.

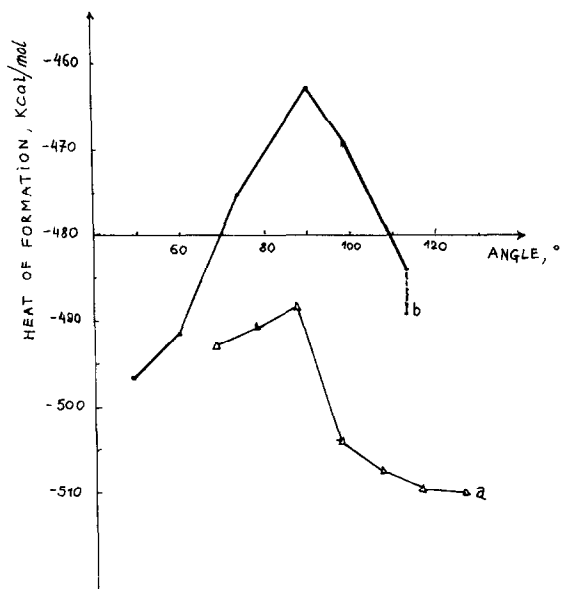


Fig. 6. Energy profiles for dissociation of HCOOH (a) by scheme 1 and (b) by scheme 2.

sites, respectively. In the former case of reaction channel (2) such a reaction coordinate correspond to the COZn angle formed between the C–O bond of HCOOH and the Zn–O(H) bond: it is equal to 114.1° and 48.9° for molecular and dissociative adsorption of HCOOH on the same pair of two-coordinated sites, respectively. Note that, however, an unidentate structure for molecular adsorption of HCOOH via its O atom of the C–O group is found unstable by 3.0 kcal/mol compared to an isolated cluster and HCOOH (Table 1). So in this case, the adsorption complex shown in Fig. 3a is taken as an initial state for molecular adsorption. Fig. 6 shows the energy profiles for these two reaction channels. As is expected the reaction channel (1) is found energetically more favourable compared to reaction channel (2) and their energy barrier amounts to 4.8 and 24.6 kcal/mol, respectively.

3.3. Interaction of HCOOH with small clusters

In Section 3.1 and Section 3.2, we presented the results obtained by using relatively large

Zn₁₆O₁₆ cluster model for zinc oxide. To clarify the effects of a next-neighbour pair of two-coordinated acid and base centres on the energetics of these adsorptive interaction processes we had been performed some additional calculations using small Zn₄O₄ cluster model. Of course, this is not the case for real zinc oxide, where the quantity of a next-neighbour two-coordinated pair of acid and base sites is much less than that of three-coordinated sites. Nevertheless, it is of special theoretical interest. In our case, we have both three- and two-coordinated acid and base centres. Since total optimization of geometry of Zn₄O₄ cluster leads to a strongly distorted structure, the geometry of this cluster were fixed at the values corresponding to the experimental bulk structure of ZnO, i.e., the Zn–O bond length were set equal to 1.9733 Å, OZnO angles were set equal to 108.1°. We found that molecular adsorption energies of *cis*-HCOOH equals 10.0, 9.4 and 6.1 kcal/mol, respectively to form unidentate, bidentate and bridge structures. For the molecular adsorption of *trans*-HCOOH, adsorption energies amount to 10.8, 2.3 and 10.1 kcal/mol to form a six- and a four-membered structures on a next-neighbour pair of Zn_{2C}²⁺–O_{2C}²⁻ sites and a six-membered structure on the distant Zn_{2C}²⁺–O_{2C}²⁻ acid–base centres, respectively. As is clear, molecular adsorption of *trans*-HCOOH is little favoured by energetics above *cis*-HCOOH. However, dissociative adsorption of *trans*-HCOOH proceeds with an essential gain in energy. For example, dissociative adsorption energies of *trans*-HCOOH equals 45.4, 40.6 and 40.3 kcal/mol to form a bridge, a bidentate and an unidentate structures, respectively.

3.4. Cluster size effect

Since dissociative adsorption of HCOOH proceeds with an essential stabilization of the dissociated fragments on a next-neighbour two-coordinated acid–base pair of centres of (10 $\bar{1}$ 0) surface of zinc oxide it is also interesting to

Table 5

Optimized geometries (bond lengths in Å, angles in degrees) and heats of dissociative adsorption (Δ, kcal/mol) of HCOOH on Zn_{2C}²⁺–O_{2C}²⁻ pair centres of nonpolar (10 $\bar{1}$ 0) surface of zinc oxide modelled by Zn_nO_n with n = 4, 9, 16, 25, 36, 49 as calculated by MINDO/3 method

Parameter	n = 4	n = 9	n = 16	n = 25	n = 36	n = 49
Zn–O	1.899	1.908	1.915	1.915	1.916	1.916
O _s ZnO ^a	135	132	130	129	128	129
C–O	1.302	1.297	1.295	1.294	1.293	1.293
ZnOC	120	124	126	127	127	127
C=O	1.220	1.220	1.221	1.221	1.221	1.221
OCO	132	133	133	134	134	134
C–H	1.150	1.151	1.153	1.154	1.154	1.154
HCO	108	108	108	108	108	108
Δ ^b	40.3	37.8	35.3	34.6	34.2	34.2

^a Subscript (s) relates to the surface oxygen atom.

^b (+) Sign corresponds to stabilization of the dissociated fragments.

examine the influence of the cluster size on the energetics of such a process. In this case, the four-layer molecular clusters of Zn_nO_n where n = 4, 9, 16, 25, 36, 49 were used. Note that for all these clusters, the initial geometry is fixed again at the values corresponding to the experimental bulk structure of ZnO as in Section 3.3, while the internal coordinates of adsorbate molecule were fully optimized.

Table 5 shows optimized geometry characteristics and adsorption energies of HCOOH forming an unidentate formate anion structure on these clusters. As is clear, the transition from a Zn₁₆O₁₆ to Zn₄₉O₄₉ cluster does not lead to a large change in both geometries and adsorption energies of the adsorption complexes. For example, the adsorption energy difference correspond only to 3.1% when one compare adsorption complexes on Zn₁₆O₁₆ and Zn₄₉O₄₉ clusters. An analysis of the highest occupied molecular orbital (HOMO) of these clusters shows that HOMO consists preferably of 2p-AO of three-coordinated oxygen atoms for Zn₁₆O₁₆ and larger cluster models while it is 60% and 37% of 2p-AO of two-coordinated oxygens for Zn₄O₄ and Zn₉O₉ cluster models, respectively. This means that the closely placed two-coordinated acid and base centres quite strongly affects the energetics of adsorption complexes. Zn₁₆O₁₆ would be the smallest cluster which can cor-

rectly describe the adsorption interactions on the (10 $\bar{1}$ 0) surface of zinc oxide.

4. Summary

On the nonpolar (10 $\bar{1}$ 0) surface of zinc oxide, molecular adsorption of *cis*- and *trans*-HCOOH proceeds with forming an unidentate complex on a coordinatively unsaturated Zn_{2C}²⁺ site and a six-membered structure on a next-neighbour pair of Zn_{2C}²⁺–O_{2C}²⁻ acid–base centres, respectively. However, dissociative adsorption of HCOOH via forming formate anion and proton leads to a substantial gain in energy. In this case, the proton is connected to a basic site while a bridge or a bidentate structure is energetically more favourable for a formate anion compared to an unidentate structure.

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