

Adsorption of methanol, formaldehyde and formic acid on the Si(100)-2 × 1 surface: A computational study

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The adsorption of methanol, formaldehyde and formic acid on the Si(100)-2 × 1 surface have been investigated by means of first-principles density functional cluster model calculations and *ab initio* ONIOM calculations. The dissociative adsorption of methanol on the Si(100) surface takes place readily, giving rise to Si–OCH₃ and Si–H surface species. The reaction, occurring barrierlessly *via* a stable chemisorbed state and the transition state for dissociation, is highly exothermic. The chemisorption of formaldehyde on the Si(100) surface is also barrierless and exothermic with the formation of a 4-member ring –SiCOSi– surface species. This result indicates that the carbonyl (C=O) group can undergo cycloaddition onto the Si dimer on the Si(100) surface. The dissociative chemisorption of formic acid occurs readily on the Si(100) surface with the formation of unidentate formate surface species and H adatoms. Its exothermicity is higher than 60 kcal mol^{–1}. The vibrational frequencies of the surface species produced by the chemisorption of the three C₁ molecules have been calculated and compared with the available experimental data.

1. Introduction

The chemistry of organic molecules on Si surfaces is not only of interest from the fundamental perspective, but is also of technological importance.^{1,2} Small organic molecules on Si surfaces serve as model systems in studies of the process of SiC, SiN, SiO and thin diamond film formation on the surfaces.^{1–6} While the interaction of alkenes and alkanes with Si surfaces has received extensive attention from both the experimental^{1–11} and theoretical communities,^{12–18} less attention was paid to the chemistry of alcohol,^{19–23} aldehyde^{24–26} and carboxylic acid^{27–30} on Si surfaces until more recently.

In the present work, we have studied the interaction of three C₁ organic molecules, methanol (CH₃OH), formaldehyde (CH₂O) and formic acid (HCOOH), with the reconstructed Si(100)-2 × 1 surface by the use of density functional (DFT) cluster model calculations and a two-layer ONIOM approach. The work was motivated by the following reasons: (i) There is no systematic theoretical work so far reported on the chemistry of alcohol, aldehyde and carboxylic acid on Si surfaces. (ii) It is interesting to examine the different behaviors of the three types of organic molecules on Si surfaces due to their different functional groups. (iii) The Si(100) and the three C₁ organic molecules are relatively simple systems.

Experimentally, the reaction of methanol with both porous silicon and hydrogen-covered porous silicon was investigated by means of FTIR spectroscopy.¹⁹ It was proposed that the adsorption of methanol onto porous silicon at 300 K resulted in cleavage of the O–H bond and formation of Si–OCH₃ and Si–H surface species, and heating of these surface species to ~500 K caused the breakage of both the C–O and C–H bonds.¹⁹ Similar results were obtained in the experimental studies of methanol adsorption on the Si(111) surface²³ and the hydrogen-terminated silicon surface^{31,32} and of ethanol adsorption on the Si(100) surface^{20,21} and porous silicon.²² A

recent vibrational study of ethanol adsorption on the Si(100) surface confirmed theoretically the adsorption-induced formation of Si–OC₂H₅ surface species by means of *ab initio* cluster calculations.²⁰

To the best of our knowledge, neither theoretical nor experimental work can be found in the literature concerning the reaction of formaldehyde with the Si(100) surface. Some relevant studies so far reported are those regarding the reactions of acetaldehyde,^{24,25} acetone,²⁵ biacetyl²⁶ and ketene³³ on the Si(100) surface. The experiments revealed similar surface chemistries for these carbonyl-containing organic molecules. The initial adsorption occurred through strong interactions with the carbonyl, leading to partial reduction of the C–O bond order and the complete cleavage of the C–O bond across the Si–Si dimer; subsequent decomposition of the aliphatic substituents invariably resulted in silicon carbide formation.^{24–26}

The adsorption of formic acid on the Si(100) surface was investigated by means of high resolution electron energy loss spectroscopy (HREELS),²⁷ photo-simulated ion desorption (PSID)²⁸ and surface near-edge X-ray absorption fine structure (NEXAFS)²⁹ techniques. The experimental results suggested that formic acid was partially dissociated to form the unidentate formate (HCOO) species and H adatoms on the Si surface at both 90 and 300 K.^{27–29} On the other hand, a new photoelectrochemical reaction that involves the light-induced reactions of porous and single crystal Si surfaces with carboxylic acids producing a Si surface modified with formic and acetic ester species was reported by Lee *et al.*³⁰

As alluded to above, the adsorption mechanism and the energetics of the three C₁ molecules on the Si(100) surface remain unclear. The objective of the present theoretical study is three-fold: (i) to elucidate the adsorption mechanism of methanol, formaldehyde and formic acid with the reconstructed Si(100)-2 × 1 surface, (ii) to predict the corresponding energetics theoretically and (iii) to elucidate the relationship

between their different adsorption behavior and the different functional groups.

2. Computational details

A Si_9H_{12} surface model has been used to represent the reconstructed $\text{Si}(100)\text{-}2 \times 1$ surface. Its top layer consists of two Si atoms forming a Si-Si dimer. Despite the simplicity in that it neglects the interaction between the adjacent dimers, this cluster model has been shown to give reasonable energetic and geometric predictions.^{12,15,17,34–36}

All calculations were performed with the GAUSSIAN 98 packages.³⁷ The hybrid density functional method including Becke's 3-parameter nonlocal-exchange functional³⁸ with the correlation functional of Lee–Yang–Parr³⁹ (B3LYP) was employed. The basis set used is the standard all-electron split-valence basis set 6-31G* including the polarization d-function on non-hydrogen atoms.⁴⁰ Geometry optimizations and vibrational analyses were performed without artificial geometric constraints. Unscaled zero-point-energies (ZPE) were evaluated at the B3LYP/6-31G* level.

Finally, in order to obtain more reliable energies, two-layer ONIOM(CCSD(T)/6-31G* : B3LYP/6-31G*)⁴¹ single-point calculations were performed with the geometry optimized at the B3LYP/6-31G* level. In these ONIOM calculations, the high-level part consisting of the adsorbate, the Si-Si dimer and the added H atoms were treated at the CCSD(T) level⁴² of theory employing the 6-31G* basis set. In principle, the geometry should be better fully re-optimized with the ONIOM algorithm.⁴¹ However, geometry optimization at the ONIOM(CCSD(T)/6-31G* : B3LYP/6-31G*) level would be computationally formidable. On the other hand, we believe that for most of the cases, molecular geometry obtained at the B3LYP level should be in reasonable agreement with that obtained at the CCSD(T) level.⁴³ Accordingly, we did not re-optimize the geometry with the ONIOM algorithm in the ONIOM calculations.

3. Results and discussion

3.1. Methanol

For CH_3OH adsorption on the $\text{Si}(100)$ surface, two local minima (LM1 and LM2), as well as a transition state (TS) that connects the two local minima, have been located in our calculations at the B3LYP/6-31G* level. The energy profile is depicted in Fig. 1. The calculated geometric parameters at the stationary points along the reaction pathway are given in Table 1, together with the relative energies of these points.

The first local minimum, LM1, is a molecular adsorption state, as indicated by the calculated geometric parameters

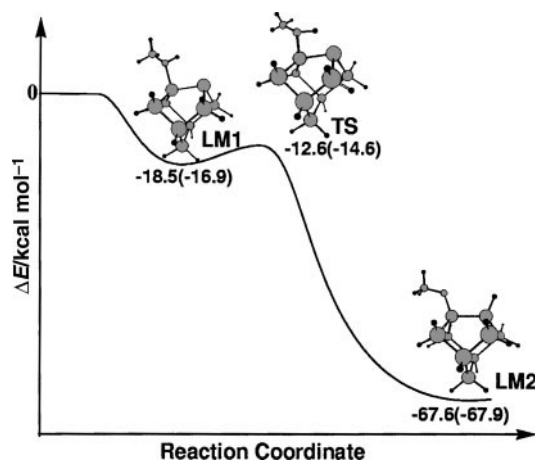


Fig. 1 Potential energy profile for the CH_3OH adsorption on the $\text{Si}(100)\text{-}2 \times 1$ surface calculated at the B3LYP/6-31G* level of theory using the Si_9H_{12} cluster model. (Energies given in parentheses are ZPE corrected values.)

given in Table 1. The geometry of the adsorbed CH_3OH species is slightly changed from that of free CH_3OH ; the intermolecular Si-O distance is 1.970 Å. Further natural bond orbitals (NBO) analysis⁴⁴ of the wavefunctions of the model system reveals a dative bond formed between the lone-pair on the O atom of the hydroxy group and the empty, anti-bonding orbital localized on the Si dimer. The strength of the orbital interaction can be estimated by the perturbative analysis of the Fock matrix in the NBO basis, and the energy contribution owing to the dative interaction is substantial ($99.2 \text{ kcal mol}^{-1}$). Such dative bonding results in a positively charged CH_3OH adspecies (with a Mulliken charge of +0.22 e) as well as an elongation (by $\sim 0.12 \text{ Å}$) of the Si-Si bond. On the other hand, the electrostatic interaction between the electron negative oxygen atom and the positively charged silicon atom (buckled-down) caused by the buckling of the Si dimer also contributes to the CH_3OH -surface binding. A similar molecular adsorption state was found in a previous DFT study of H_2O adsorption on $\text{Si}(100)\text{-}2 \times 1$ by Konecny and Doren.³⁵ Furthermore, the formation of LM1 from free CH_3OH is found to be barrierless and exothermic. At the B3LYP/6-31G* level, the formation energy of LM1 is exothermic by 18.5 (16.9) kcal mol^{-1} before (after) ZPE corrections. The two-layer ONIOM calculation predicts a lower exothermicity of 12.5 kcal mol^{-1} with ZPE corrections.

The local minimum at LM2 is a dissociative adsorption state, as shown by the large H-O distance and the formation of Si-O CH_3 and Si-H surface species (*cf.* Table 1 and Fig. 1).

Table 1 Selected structural parameters^a and relative energies^b at the stationary points along the reaction coordinate for methanol adsorption on the Si_9H_{12} cluster model of the $\text{Si}(100)\text{-}2 \times 1$ surface

Parameter	Reactant	LM1	TS	LM2
Si-Si	2.222	2.345	2.365	2.392
Si-O		1.970	1.833	1.678
O-H	0.967	0.987	1.212	3.528
C-O	1.381	1.457	1.445	1.421
Si-H		2.818	1.934	1.492
Si-Si-O		96.9	83.6	109.1
Si-O-H		102.1	89.4	67.5
Si-O-C		125.8	129.9	123.6
C-O-H	108.7	112.7	121.8	169.0
Si-Si-O-H		7.8	3.9	0.0
C-O-Si-Si		137.8	123.3	180.0
ΔE^c B3LYP	0.0	-18.5(-16.9)	-12.6(-14.6)	-67.6(-67.9)
ONIOM ^d	0.0	-14.1(-12.5)	-6.4(-8.4)	-64.5(-64.8)

^a Distances in Å and angles in degrees. ^b $\Delta E = E(\text{CH}_3\text{OH}/\text{Si}_9\text{H}_{12}) - E(\text{CH}_3\text{OH}) - E(\text{Si}_9\text{H}_{12})$, in kcal mol^{-1} . ^c Unscaled zero-point-energy (ZPE) corrected values are given in parentheses. ^d Relative energies calculated with 2-layer ONIOM(CCSD(T)/B3LYP) calculations.

The optimal length of the forming Si–O bond is 1.678 Å; the Si–H bond length is 1.492 Å. The Si–Si bond length increases by 0.14 Å due to saturation of the dangling bonds by $-\text{OCH}_3$ and $-\text{H}$ surface species. The dissociative chemisorption of CH_3OH is highly exothermic with the predicted overall reaction energies being -67.9 (-67.6) kcal mol^{-1} at the B3LYP/6-31G* level and -64.8 (-64.5) kcal mol^{-1} at the ONIOM(CCSD(T)/6-31G* : B3LYP/6-31G*) level with (without) ZPE corrections. Similarly, previous theoretical studies revealed the dissociative chemisorption of H_2O on Si(100)- 2×1 surface is thermodynamically favorable with the predicted exothermicity ranging from 49 to 63 kcal mol^{-1} depending on the density functionals and basis sets used.³⁵

We further found that the dissociative state, LM2, can only be formed from the molecular adsorption state, LM1, via a transition state, TS. With respect to LM1, the barrier at TS is predicted to be 2.3 (5.9) kcal mol^{-1} at the B3LYP/6-31G* level after (before) ZPE corrections and 4.1 (7.7) kcal mol^{-1} at the ONIOM level with (without) ZPE corrections. Nevertheless, the fact that the transition state is at least 6.4 kcal mol^{-1} lower in energy than the reactants, *i.e.*, free CH_3OH + bare cluster, suggests that the molecular adsorption state (LM1) is metastable and the dissociative chemisorption of CH_3OH can readily take place at the Si dimer sites on the Si(100)- 2×1 surface. This prediction is in line with the experimental observations by Glass *et al.* regarding the methanol reaction with porous silicon.¹⁹ Using FTIR spectroscopy, they found that adsorption of methanol onto porous silicon at 300 K resulted in cleavage of the O–H bond and formation of Si– OCH_3 and Si–H surface species.¹⁹ Another vibrational study reported by Eng *et al.* also disclosed that ethanol dissociatively adsorbed across the Si(100) dimers near room temperature to form surface bound hydrogen and ethoxy groups.²⁰

We can compare our calculated vibrational frequencies of the Si– OCH_3 and Si–H surface species with the experimental FTIR data extracted from Glass *et al.*'s work.¹⁹ The calculated and experimental vibrational frequencies of free CH_3OH ⁴⁵ and the Si– OCH_3 and Si–H surface species are given in Table 2. We found a good agreement between the calculated values and the experimental ones, confirming the assignments of Glass *et al.* from their experimental HREELS spectra.

3.2. Formaldehyde

Fig. 2(a) shows the equilibrium geometry for CH_2O adsorption on the Si dimer optimized at the B3LYP/6-31G* level of theory. Formaldehyde chemisorbs with its carbonyl group being di- σ -bonded onto the Si dimer, giving rise to the formation of a close, 4-member $-\text{SiCOSi}-$ ring. The optimal intermolecular Si–O and Si–C bond lengths are predicted to be

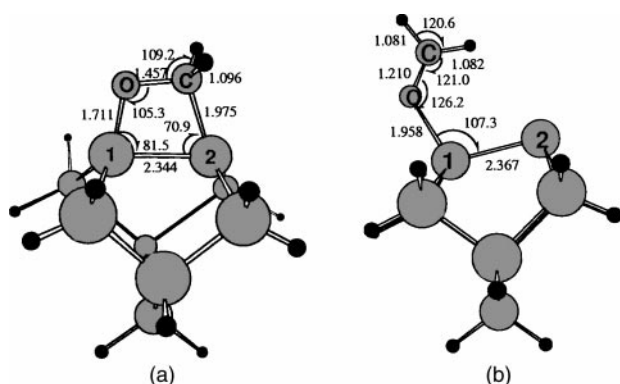


Fig. 2 CH_2O adsorption on the Si_9H_{12} cluster, (a) di- σ -bonded CH_2O optimized at the B3LYP/6-31G* level of theory (dihedral angle $\angle \text{H-C-O-Si} = 120.8^\circ$); (b) singly bonded CH_2O optimized at the HF/6-31G* level (no local minimum at the B3LYP/6-31G* level).

1.711 and 1.975 Å, respectively. Upon chemisorption, the C–O bond in CH_2O and the Si–Si bond of the Si dimer are elongated by 0.25 and 0.12 Å, respectively. The geometrical change indicates the chemisorption-induced reduction of bond order of the C–O bond and of the Si–Si dimer. Furthermore, the formation of the di- σ -bonded surface species is found to be barrierless and rather exothermic. The process is initiated by a nucleophilic attack of the O-end of formaldehyde onto the positively charged, buckled-down Si atom of the Si–Si dimer. The predicted chemisorption energies are -48.9 (-52.1) kcal mol^{-1} at the B3LYP/6-31G* level and -42.2 (-45.4) kcal mol^{-1} at the ONIOM(CCSD(T)/6-31G* : B3LYP/6-31G*) level with (without) ZPE corrections. Similar to the methanol case, the ONIOM prediction for the adsorption energy is several kcal mol^{-1} lower than the B3LYP value.

Besides the aforementioned 4-member ring chemisorption state, we have considered another possible adsorption configuration, in which formaldehyde is singly bonded onto the buckled-down Si atom of the Si–Si dimer with the formation of a planar CH_2OSi_2 surface species (see Fig. 2(b)). However, we could not locate such a local minimum at the B3LYP/6-31G* level of theory. Instead, we obtained an equilibrium geometry at the HF/6-31G* level. The optimal geometry is given in Fig. 2(b). The adsorption energy predicted by single-point B3LYP/6-31G* calculation at the HF/6-31G* optimized geometry is -12.1 kcal mol^{-1} , showing that the adsorption state, if it exists, is much weaker than the 4-member ring chemisorption state. Furthermore, no transition state could be located between the two adsorption states at either the B3LYP/6-31G* or the HF/6-31G* level of theory. It seems that the barrier, if it exists, is rather low for the transformation from the weak adsorption state to the strong one.

By means of TPD, XPS and HREELS, Armstrong *et al.* examined the thermal reactions of acetaldehyde, acetone and biacetyl, all carbonyl-containing molecules, on the Si(100) surface.^{25,26} They proposed that the initial adsorption of these molecules could occur through strong interactions with the carbonyl functional group, leading to either the reduction of the carbonyl bond order to form a di- σ -bonded species, or the complete cleavage of the C=O bond. Bu *et al.* obtained similar results for the adsorption of acetaldehyde on the Si(111) surface.²⁴ We have confirmed herein the chemisorption-induced bond-order reduction of the carbonyl C=O bond. Furthermore, we suspect that for the di- σ -bonded H_2CO , the C–O bond can be further cleaved at elevated temperatures to form CH_2 (a) and O(a) adspecies. O(a) adspecies may cause partial oxidation of the surface by inserting into the Si–Si backbond with severe reconstruction of the surface.⁴⁶ This process is unlikely to be reasonably simulated by the simple Si_9H_{12} cluster.

Furthermore, our results provide the first theoretical evidence that, similar to the cycloaddition of formaldehyde to ethylene that leads to the formation of oxetane,⁴⁷ a C=O bond can also undergo [2 + 2] addition onto the Si–Si dimer of the Si(100)- 2×1 surface. Apart from the present formaldehyde study, it was theoretically demonstrated that molecules containing groups of multibonds, such as $\text{C}\equiv\text{C}$ (*e.g.* C_2H_2),^{12–15} $\text{C}=\text{C}$ (*e.g.* C_2H_4),¹⁵ $\text{C}=\text{N}$ (*e.g.*, phenyl isothiocyanate),⁴⁸ $\text{C}\equiv\text{N}$ (*e.g.* HCN),⁴⁹ $\text{N}=\text{N}$ (*e.g.*, HN_3 and azo-*tert*-butane)^{50,51} and $\text{N}=\text{C}=\text{S}$ (*e.g.*, phenyl isothiocyanate)⁴⁸ can undergo cycloaddition reactions on the Si(100) surface, giving rise to di- σ -bonded surface species. It is a fascinating and noteworthy feature that the Si–Si dimer of the Si(100)- 2×1 surface can readily undergo cycloaddition with adsorbates containing double or triple bonds; this opens up ways to functionalize silicon surfaces in a specific, desired pattern and, hence, may be one of the keys to making usable molecular wires and new molecule-scale devices.²

The calculated vibrational frequencies of adsorbed and free CH_2O are listed in Table 3, together with the experimental

Table 2 Calculated^a and experimental vibrational frequencies (cm⁻¹) of free CH₃OH and of the Si–OCH₃ and Si–H surface species in the CH₃OH/Si(100) chemisorption system

Normal mode	CH ₃ OH		CH ₃ OH/Si(100)	
	Expt. ^b	Calc.	Expt. ^c	Calc.
CH ₃ d-str.	3000	3007	2971	3001
	2960	2916	2946	2947
CH ₃ s-str.	2844	2876	2844	2893
CH ₃ d-deform.	1477	1480		1466
	1477	1464	~1461	1463
CH ₃ s-deform.	1455	1452	1447	1449
OH bend.	1345	1343	—	—
CH ₃ rock.	1165	1135	1182	1164
	1060	1055		1138
C–O str.	1033	1027	—	—
Si–O–C a-str.	—	—	1086	1068
Si–O–C s-str.	—	—	800 ^c	742
Si–H str.	—	—	2091	2127

^a Calculated at the B3LYP/6-31G* level and scaled by 0.96. ^b Ref. 44. ^c Ref. 32.

values of free CH₂O.⁴⁵ It is notable that the C–O bond stretch frequency shows a significant red-shift from 1778 to 953 cm⁻¹ upon chemisorption. Meanwhile, the C–H bond stretch frequencies of the CH₂ group shift from 2850 (asymmetric CH₂ stretch) and 2800 (symmetric CH₂ stretch) cm⁻¹, which are typical for CH_x species with an sp² C atom, to 2979 and 2931 cm⁻¹, which are typical for CH_x species with an sp³ C atom, respectively. As such, we believe that such considerable shifts of C–O and CH₂ stretch frequencies can be fingerprints of the di-σ-bonded CH₂O in future experimental vibrational analysis of the CH₂O/Si(100) system.

3.3. Formic acid

At the B3LYP/6-31G* level, we have found four local minima, LM1'–LM4', for HCOOH adsorption on the Si–Si dimer, as depicted in Fig. 3. In addition, a transition state, TS', was located to connect LM1' and LM2' (see Fig. 3). The relative energies and geometric parameters of these five stationary points are given in Table 4, together with the optimized geometry of the free HCOOH molecule.

Both LM1' and LM4' are physisorption states in which HCOOH is weakly attached onto the buckled-down Si atom through the hydroxy O atom and the carbonyl O atom, respectively. The corresponding Si–O distance is 2.172 Å for LM1' and 1.984 Å for LM4'. The adsorption energy is –3.1 kcal mol⁻¹ for LM1' and –11.8 kcal mol⁻¹ for LM4', respectively, predicted at the B3LYP/6-31G* level including ZPE corrections. With the 2-layer ONIOM approach, the adsorption is predicted to be energetically unfavorable for LM1' and rather weak for LM4' (*cf.* Table 4). We are not sure if LM1' is an artifact of the method employed. Nevertheless, neither LM1' nor LM4' could be practically significant to the

Table 3 Calculated^a and experimental vibrational frequencies (cm⁻¹) of free CH₂O and of the CH₂O adsorbed on the Si(100)-2 × 1 surface

Normal mode	CH ₂ O		CH ₂ O/Si(100)
	Expt. ^b	Calc.	Calc.
CH ₂ a-str.	2843	2850	2979
CH ₂ s-str.	2783	2800	2931
CO str.	1746	1778	953
CH ₂ scis.	1500	1500	1441
CH ₂ rock.	1249	1227	1220
CH ₂ wag.	1167	1150	1156
Si–CH ₂ rock.	—	—	755
O–Si str.	—	—	750

^a Calculated at the B3LYP/6-31G* level and scaled by 0.96. ^b Ref. 44.

HCOOH/Si(100) chemisorption system, as suggested by their rather low binding energies in comparison with the high binding energies of the other chemisorbed states, LM2' and LM3', to be considered in the following paragraph.

One may consider LM1' as a precursor state; O–H cleavage may occur in a similar way to that of the CH₃OH dissociative adsorption on Si(100) described above. Accordingly, we located a dissociative state LM2' and a transition state TS' that is responsible for the LM1' → LM2' transformation. At the B3LYP/6-31G* level, the barrier at TS' is 2.2 kcal mol⁻¹ (including ZPE corrections) with respect to LM1'. A slightly higher barrier is predicted at the ONIOM(CCSD(T): B3LYP) level, *i.e.*, 3.8 kcal mol⁻¹ with respect to LM1' and 9.2 kcal mol⁻¹ with respect to free reactants with ZPE corrections. However, whether there exists TS' between LM1' and LM3' and the height of the barrier at TS' are not important for the formation of LM2'. We found that LM2' can be formed barrierlessly from the reactants in a concerted way. That is, along with the formation of the Si–O bond between the buckled-down Si atom and the carbonyl O atom of HCOOH, the cleavage of hydroxy O–H bond by the buckled-up Si atom occurs simultaneously, leading to the formation of unidentate formate and H adspecies on the Si–Si dimer. The formation of the dissociative adsorption state LM2' is rather exothermic; the predicted formation energy is –66.3 (–65.6) kcal mol⁻¹ at the B3LYP/6-31G* level and –61.9 (–61.2) kcal mol⁻¹ at

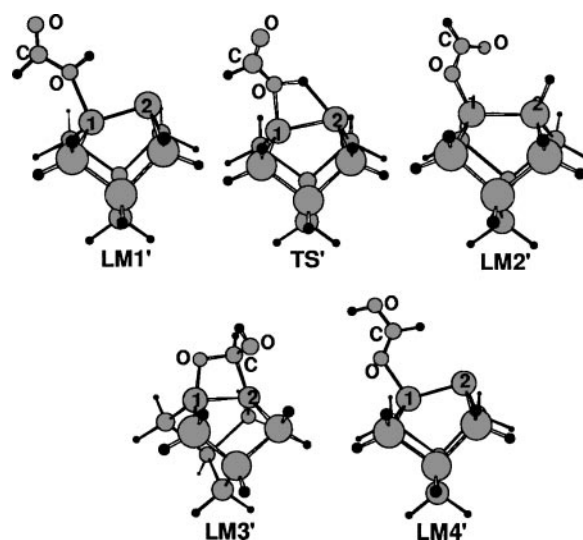
**Fig. 3** The geometry of adsorption states and transition state for HCOOH adsorbed on Si₃H₁₂.

Table 4 Selected structural parameters^a and relative energies^b at the stationary points for formic acid adsorption on the Si₉H₁₂ cluster model of the Si(100)-2 × 1 surface

Parameter	Reactant	LM1'	TS'	LM2'	LM3'	LM4'
Si-Si	2.222	2.324	2.363	2.393	2.343	2.358
Si-O		2.172	1.920	1.744	1.719	1.984
Si-C					1.981	
O-H	0.978	0.987	1.172	3.729	0.974	0.980
C-O	1.347	1.387	1.388	1.340	1.401	1.308
	1.205	1.192	1.192	1.210	1.451	1.240
C-H	1.100	1.096	1.100	1.100	1.098	1.095
Si-H		3.054	2.016	1.490		
Si-Si-O		96.6	82.7	114.8	81.1	107.5
Si-O-H		107.3	91.0	61.8		
Si-O-C		137.9	137.5	118.9	105.4	123.3
C-O-H	109.6	111.7	123.5	78.5	107.5	109.6
O-C-O	125.2	122.9	122.9	125.0	110.9	122.1
H-C-O	109.3	109.1	110.3	110.9	106.6	122.9
Si-Si-O-H		1.7	1.0	1.3		0.0
C-O-Si-Si		158.9	147.8	57.7	-6.8	0.0
O-C-O-Si		-159.6	-156.7	-0.1	-106.4	180.0
H-C-O-Si		20.9	23.4	179.9	132.0	0.0
ΔE ^c B3LYP	0.0	-3.4(-3.1)	2.2(-0.9)	-65.6(-66.3)	-28.8(-26.7)	-13.9(-11.8)
ONIOM ^d	0.0	5.1(5.4)	12.3(9.2)	-61.2(-61.9)	-24.0(-21.9)	-5.1(-3.0)

^a Distances in Å and angles in degrees. ^b ΔE = E(HCOOH/Si₉H₁₂) - E(HCOOH) - E(Si₉H₁₂), in kcal mol⁻¹. ^c Unscaled zero-point-energy (ZPE) corrected values are given in parentheses. ^d Relative energies calculated with the 2-layer ONIOM(CCSD(T)/6-31G*: B3LYP/6-31G*) approach.

the ONIOM(CCSD(T)/6-31G*: B3LYP/6-31G*) level with (without) ZPE corrections. The forming Si-O and Si-H bond lengths are 1.744 and 1.490 Å, respectively. The HCOO-Si species is nearly planar with its HCOO plane tilted away from the surface normal by about 23°. This prediction confirms the recent NEXAFS measurements²⁹ that the molecular plane of the adsorbed format group is tilted away from surface normal by an average angle of 21 ± 2°.

LM3', resembling the chemisorption state of CH₂O, is formed by cycloaddition of the C=O group onto the Si-Si dimer. Its formation energy is -26.7 (-28.8) kcal mol⁻¹ at the B3LYP/6-31G* level and -21.9 (-24.0) kcal mol⁻¹ at the ONIOM(CCSD(T)/6-31G*: B3LYP/6-31G*) level with (without) ZPE corrections, considerably lower than that of the CH₂O case (*i.e.*, -52.1 kcal mol⁻¹ at the B3LYP/6-31G* level).

Among the four adsorption states considered, LM2' is the most favorable both thermodynamically and kinetically. This is in line with the experimental observation^{27,29} that formic acid is partially dissociated to form the unidentate formate species and H adatoms on the Si(100) and (111) surfaces at 90 and 300 K, respectively. In Table 5, the calculated and experimental vibrational frequencies of the HCOO-Si and H-Si surface species and of free HCOOH⁴⁵ are tabulated. The

experimental data were extracted from the work of Tanaka *et al.*²⁷ It can be seen that our theoretical values are in good agreement with Tanaka's HREELS data.

4. Concluding remarks

We have applied the hybrid density functional B3LYP and the ONIOM methods using a single dimer cluster model to study the mechanisms for adsorption of methanol, formaldehyde and formic acid on the Si(100)-2 × 1 surface. The following remarks can be made.

(i) Methanol undergoes dissociative adsorption on the Si dimer of the Si(100) surface without an intrinsic activation barrier, giving rise to Si-OCH₃ and Si-H surface species. A molecular precursor state and a transition state are also revealed in the reaction pathway of the dissociative process. The reaction is found to be exothermic by -67.9 kcal mol⁻¹ at the B3LYP/6-31G* level and -64.8 kcal mol⁻¹ at the ONIOM(CCSD(T)/6-31G*: B3LYP/6-31G*) level. The reaction seems more exothermic than the dissociative adsorption of H₂O on the same surface.

(ii) The chemisorption of formaldehyde on the Si(100) surface leads to the formation of di-σ-bonded carbonyl group.

Table 5 Calculated^a and experimental vibrational frequencies (cm⁻¹) of free HCOOH and of the HCOO-Si and H-Si species in the HCOOH/Si(100) surface

Normal mode	HCOOH		HCOOH/Si(100)	
	Expt. ^b	Calc.	Expt. ^c	Calc.
OH str.	3570	3515	—	—
CH str.	2943	2964	2920	2953
C=O str.	1770	1784	1730	1722
CH bend.	1380	1365	1360	1348
	1033	1012		1000
OH bend.	1229	1272	—	—
C-O str.	1105	1103	1190	1154
OCO deform.	625	601	710	744
Torsion	638	681	—	—
Si-O	—	—	710	685
Si-H	—	—	2110	2122

^a Calculated at the B3LYP/6-31G* level and scaled by 0.96. ^b Ref. 44. ^c Ref. 27.

This cycloaddition process is found to be barrierless and initiated by a nucleophilic attack of the O-end of CH₂O on to the positively charged, buckled-down Si atom of the Si–Si dimer. Its exothermicity is predicted to be 48.9 kcal mol⁻¹ at the B3LYP/6-31G* level and 42.2 kcal mol⁻¹ at the ONIOM(CCSD(T)/6-31G* : B3LYP/6-31G*) level. The result provides the first theoretical evidence that the carbonyl (C=O) group can undergo cycloaddition onto the Si dimer of the Si(100)-2 × 1 surface.

(iii) Dissociative chemisorption of formic acid occurs readily on the Si dimer with the possible existence of several weak, molecular adsorption states. Unidentate formate surface species and H adatoms are thus formed. The exothermicity of the dissociative adsorption is predicted to be higher than 60 kcal mol⁻¹.

We have calculated the vibrational frequencies of the adsorbed species for the chemisorption systems and compared them with the available experimental data. The agreement between the theoretical and experimental values is quite good. Finally, whether other alcohols, aldehydes and carboxylic acids with more carbon atoms would follow the chemistries described herein for these C₁ molecules is an interesting question and deserves further experimental and theoretical investigations. It is worth noting that available experimental data revealed similar chemisorptive behavior for their C₂ and C₃ homologues on the Si(100) surface.^{20,24–26,33}

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