Chemisorption and Decomposition of Thiophene and Furan on the Si(100)-2 × 1 Surface: A Quantum Chemical Study

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The chemisorption and decomposition of thiophene (C_4H_4S) and furan (C_4H_4O) on the reconstructed Si(100)-2 × 1 surface has been investigated by means of the hybrid density functional (B3LYP) method in combination with a cluster model approach. Two chemisorption mechanisms, i.e., [4 + 2] and [2 + 2] cycloadditions of C_4H_4X (X = S,O) onto a surface dimer site, have been considered comparatively. The calculations revealed that the former process is barrierless and favorable over the latter, which requires a small activation energy (2.6 kcal/mol for thiophene and 1.2 kcal/mol for furan). The di-σ bonded surface species formed by [4 + 2] cycloaddition-type chemisorption can either undergo further [2 + 2] cycloaddition with a neighboring Si=Si dimer site, giving rise to a tetra-σ bonded surface species, or undergo deoxygenation (desulfurization) by transferring the heteroatom to a neighboring Si=Si dimer site, leading to a six-member ring metallocyclic $C_4H_4Si_2$ surface species. The latter process was found to be slightly more favorable than the former, especially in the case of thiophene.

1. Introduction

The interaction of π-conjugated, aromatic compounds with silicon surfaces is not only of fundamental interest, but also of practical importance to the development of highly ordered thin-films of conducting or semiconducting polymers on silicon surfaces.[1,2] Growing efforts devoted to this topic include the experimental studies of the adsorption of benzene (C_6H_6),[3–5] pyridine (C_5H_5N),[6–8] furan (C_4H_4O),[9–12] thiophene (C_4H_4S),[9,10,13,14] and pyrrole[10] on the Si(111) and its reconstructed surfaces and the adsorption of benzene,[15–18] pyrrole,[19] and thiophene[20,21] on the Si(100)-2 × 1, as well as the theoretical studies of benzene[22–27] and pyrrole[28] adsorption on the Si(100)-2 × 1 surface. In the present paper, we report the results of first-principles density functional cluster model calculations for the chemisorption and decomposition of thiophene and furan on the Si(100)-2 × 1 surface.

The reconstructed Si(100)-2 × 1 surface has a bonding motif that pairs of atoms form dimers with a strong σ-bond and a quite weak π bond. Accordingly, these surface dimers show high reactivity toward in-coming unsaturated organic compounds, including simple alkenes, dienes, as well as benzene, as revealed by previous experimental and theoretical studies.[29] The chemistry of unsaturated organic compounds on the Si(100)-2 × 1 surface can be summarized as follows: (i) simple alkenes, e.g., ethylene and cyclopentene, undergo [2 + 2] cycloaddition reaction with the surface dimer;[23,29] (ii) conjugated dienes, e.g., 1,3-butadiene and 1,3-cyclohexadiene, undergoes both [4 + 2] cycloaddition reaction and [2 + 2] cycloaddition reaction with the surface dimer, with the former process being kinetically preferable over the latter;[30–32] (iii) chemisorption of highly π-conjugated aromatics such as benzene on the Si(100)-2 × 1

surface follows exclusively the [4 + 2] cycloaddition mechanism with the initial product being a di-σ bonded, 1,4-cyclohexadiene-like surface species.[15–18,22–27] Both thiophene and furan are five-member ring, π-conjugated compounds with a heteroatom. They differ from common conjugated dienes by showing considerable aromaticity. They are also unlike the aromatic benzene, due to its inhomogeneous electron distribution within the whole ring system. As such, they might display somewhat different, yet interesting, chemisorption behavior from that of common dienes and benzene on the Si(100)-2 × 1 surface.

The adsorbed state of thiophene on the Si(100)-2 × 1 was first investigated by Jeong et al. using LEED (low-energy electron diffraction), AES (Auger electron spectroscopy), and UPS (ultraviolet photoelectron spectroscopy).[21] The (2 × 1) LEED pattern at 300 K was sustained after saturated exposure of thiophene, and the saturation coverage was estimated to be ~0.6 by AES, suggesting that thiophene molecules is chemisorbed molecularly on the Si(100) surface most likely by σ bonds between C and Si atoms. UPS spectrum for the chemisorbed thiophene showed not only the π orbital shift but also the σ orbital shift. The authors also performed semiempirical PM3 cluster model calculations to study the chemisorption mechanism and proposed that thiophene is di-σ bonded onto a surface dimer with its 2,3 C atoms, i.e., a [2 + 2] cycloaddition mechanism.[21] This proposal is contradicted very recently by Qiao et al.,[20] who studied the same surface reaction by means of UPS, XPS (X-ray photoelectron spectroscopy), and HREELS (high-resolution electron energy loss spectroscopy). They concluded that thiophene is chemisorbed in the form of a 2,5-dihydrothiophene-like species following a [4 + 2] cycloaddition mechanism. In their experiments, two adsorption states were identified at 120 K and assigned them to a physisorbed and a chemisorbed thiophene, respectively. The physisorbed one desorbs below 200 K. Above 400 K, the chemisorbed species were found to either desorb molecularly or decompose possibly via α-thiophenyl and Si–H through a H-abstraction mechanism,

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TABLE 1: Adsorption Energies[a] and Selected Geometric Parameters of the C_4H_4X/Si_9O_{12} (X = O,S) Model Systems from B3LYP/6-31G(d) Calculations

	C_4H_4S/Si_9O_{12}				C_4H_4O/Si_9O_{12}			
	reacts.	LM1	LM2	TS1	reacts.	LM1	LM2	TS1
Si_A-Si_B (Å)	2.222	2.386	2.358	2.414	2.222	2.379	2.364	2.414
C_2-Si_A (Å)		1.965	1.959	2.063		1.993	1.967	2.094
C_3-Si_B (Å)			1.976	3.356			1.971	3.362
C_5-Si_B (Å)		1.965				1.993		
C_2-C_3 (Å)	1.368	1.509	1.588	1.453	1.361	1.503	1.584	1.440
C_3-C_4 (Å)	1.430	1.342	1.500	1.392	1.436	1.341	1.508	1.393
C_4-C_5 (Å)	1.368	1.509	1.338	1.394	1.361	1.503	1.337	1.389
C_2-X (Å)	1.735	1.857	1.863	1.814	1.364	1.442	1.454	1.436
C_5-X (Å)	1.735	1.857	1.771	1.706	1.364	1.442	1.369	1.320
$Si_B-Si_A-C_2$ (°)		92.5	78.7	105.1		88.5	78.4	106.7
$Si_A-C_2-C_5$ (°)		87.5	121.3	115.6		91.5	118.3	115.4
$Si_A-C_2-C_3$ (°)		106.7	101.9	107.0		108.4	101.7	106.3
ΔE (kcal/mol)	0.0	−34.3	−22.4	2.6	0.0	−30.0	−21.8	1.2
	(0.0)	(−36.0)	(−23.6)	(2.5)	(0.0)	(−31.6)	(−22.9)	(1.1)

[a] Adsorption energy $\Delta E = E(C_4H_4X/Si_9H_{12}) - E(Si_9H_{12}) - E(C_4H_4X)$. Energies without zero-point energy corrections are given in parentheses.

and via a metallocyclic-like intermediate and atomic S through a S-abstraction mechanism.[22] The same authors also examined the chemisorption of thiophene on the Si(111)-7 × 7 surface, and proposed that thiophene undergoes [4 + 2] cycloaddition-like chemisorption onto an adatom-rest atom pair site with the formation of a 2,5-dihydrothiophene-like adspecies.[14] Consequently, whether thiophene undergoes [2 + 2] cyclo-addition-like or [4 + 2] cycloaddition-like chemisorption on the Si(100)-2 × 1 is debatable. One of the objectives of the present theoretical study is to provide a clear-cut answer to this question and, in addition, to investigate the decomposition pathways of chemisorbed thiophene upon heating.

So far neither experimental nor theoretical work could be found in the literature regarding furan adsorption on the Si(100)-2 × 1 surface. One expects that the adsorptive behavior of furan on the Si(100)-2 × 1 surface would be similar to that of thiophene, considering their similarity in geometric and electronic structures. However, recent TDS (thermal desorption spectroscopy) and HREELS experiments revealed the dimer-ization of furan on the Si(111)-7 × 7 surface,[12] whereas no dimerization was found for thiophene on the same surface.[14] Another purpose of the present theoretical study is, therefore, to compare the chemisorption behaviors of furan and thiophene on the Si(100)-2 × 1 surface and examine the extent of their similarity in surface reactions.

Density functional theory (DFT) in combination with cluster model approach has been used for the above-mentioned purposes. This paper is organized as follows. In Section 2, we introduce the computational method and the cluster model used. In Section 3, the calculated results are presented, along with the chemisorption mechanisms of C_4H_4X (X = S,O) on the Si(100)-2 × 1 surface as well as the different pathways of thermal isomerization and decomposition of the chemisorbed C_4H_4X. Concluding remarks will be given in Section 4.

2. Computational Details

We have used two surface models to represent the recon-structed Si(100)-2 × 1 surface. The first one is a single-dimer Si_9H_{12} cluster, where the top layer is a dimer consisting of two Si atoms, each with one dangling bond.[23,27,28,31–34] The second model is a $Si_{15}H_{16}$ cluster, where the top layer consists of two adjacent dimers in the same dimer row.[34–36] The double-dimer model allows the study of chemisorption and dissociation of adsorbates across the dimer pairs. All calculations were performed with the GAUSSIAN94 package.[37] The hybrid
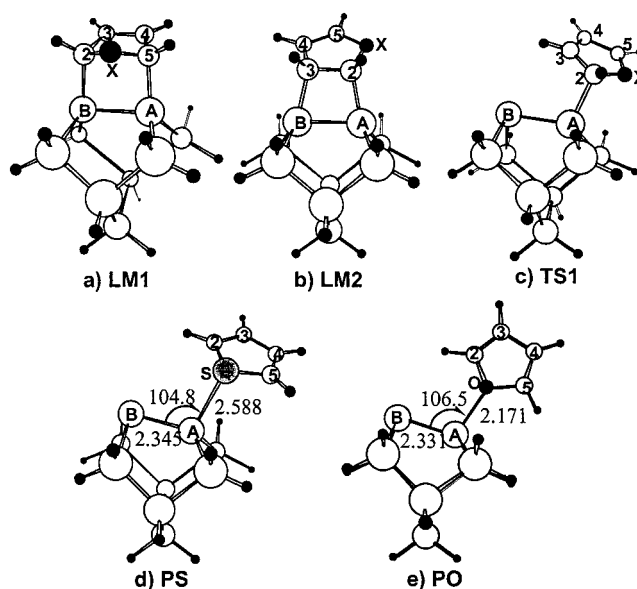

Figure 1. Local minima and transition states for the C_4H_4X/Si_9H_{12} (X = S,O) systems predicted at the B3LYP/6-31G(d) level of theory.

density functional method including Becke's 3-parameter non-local-exchange functional[38] with the correlation functional of Lee–Yang–Parr[39] (B3LYP) as well as analytical gradients was employed. The basis set used is the standard all-electron split-valence basis set 6-31G(d) including the polarization d-function on non-hydrogen atoms.[40] Geometry optimizations and vibra-tional analyses were performed without any constraint. Final energy parameters include the unscaled zero-point-energy (ZPE) corrections calculated at the B3LYP/6-31G (d) level of theory.

3. Results and Discussion

3.1. C_4H_4X (X = S,O) Chemisorption on Si_9H_{12}. As mentioned above, an earlier experimental and theoretical study suggested that thiophene chemisorption on the Si(100)-2 × 1 occurred by the [2 + 2] cycloaddition mechanism,[21] whereas a recent HREELS experiment suggested that the adsorption occurred by the [4 + 2] cycloaddition mechanism.[20] We have considered both reaction pathways in our calculations using the Si_9H_{12} cluster model. Figure 1 presents the optimized geometries of the local minima and transition states for the C_4H_4X/Si_9H_{12} model systems. The relative energies and selected geometrical parameters of various stationary points are given in Table 1.

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The [4 + 2] cycloaddition of thiophene onto the dimer site gives rise to a di-σ bonded, 2,5-dihydrothiophene-like adspecies (LM1), as shown in Figure 1a. This process is exothermic by −34.3 kcal/mol predicted at the B3LYP/6-31G(d) level of theory. Effort has been paid to search for the transition state responsible for the [4 + 2] cycloaddition process. The results revealed that this process is concerted and barrierless. In the [4 + 2] product (LM1), the length of two equivalent C−Si bonds thus-formed is 1.965 Å; the Si−Si bond length is elongated by 0.164 Å with respect to the unreacted one; the C_3−C_4 bond length is shortened to 1.342 Å, which is typical for a C=C double bond.

The [2 + 2] cycloaddition of thiophene onto the dimer site of the Si_9H_{12} cluster leads to di-σ bonded, 2,3-dihydrothiophene-like adspecies (LM2), as shown in Figure 1b. This process is exothermic by −22.4 kcal/mol predicted at the B3LYP/6-31G(d) level of theory, and is thermodynamically less favorable than the [4 + 2] cycloaddition process. In LM2, the two C−Si bond lengths are 1.959 and 1.976 Å; the Si−Si bond length is elongated by 0.136 Å with respect to the unreacted one; the C_2−C_3 bond length is elongated to 1.588 Å, which is typical for a C−C single bond. Unlike the [4 + 2] process, which is concerted and barrierless, the [2 + 2] process has a transition state (TS1) with a barrier height of 2.6 kcal/mol predicted at the B3LYP/6-31G(d) level. At TS1, the two forming C−Si bond lengths are 2.063 and 3.356 Å, showing the [2 + 2] process is not concerted. It is clear that for thiophene chemisorption onto the Si(100)-2 × 1 surface, the [4 + 2] process is both kinetically and thermodynamically favorable over the [2 + 2] process, and the barrierless [4 + 2] process can readily occur at a rather low temperature, e.g., 90 K.

Similar chemisorption behavior has been predicted for furan, as shown in Figure 1 and Table 1. A di-σ bonded, 2,5-dihydrofuran-like surface species is formed by [4 + 2] cycloaddition, whereas the [2 + 2] process results in a di-σ bonded, 2,3-dihydrofuran-like adspecies. The [2 + 2] process requires an activation energy of 1.2 kcal/mol predicted at the B3LYP/6-31G(d) level, and is kinetically less favorable than the [4 + 2] process. Both processes are exothermic with the predicted reaction energies of −30.0 and −21.8 kcal/mol for the [4 + 2] and [2 + 2] processes, respectively.

At this conjuncture, it is interesting to compare the chemisorptive behavior of thiophene and furan with that of other conjugated organic compounds such as benzene and 1,3-cyclohexadiene on the same surface. For benzene and 1,3-cyclohexadiene, previous experimental and theoretical studies revealed that both π-conjugated molecules preferentially undergo [4 + 2] cycloaddition-like chemisorption on the Si(100)-2 × 1 surface,[15–18,22–27,32] but the adsorption energy of benzene is by far lower than that of 1,3-cyclohexadiene.[23] This intriguing phenomenon can be ascribed to the aromatic stabilization in benzene. Indeed, previous B3LYP/6-31G** cluster model calculations[23] did predict a difference of 32.6 kcal/mol in binding energy between benzene and 1,3-cyclohexadiene, which is comparable to the difference (~28.3 kcal/mol)[41,42] in resonance energy between benzene and 1,3-cyclohexadiene. It is known that both thiophene and furan are aromatic compounds, but less aromatic than benzene.[41] Hence it is plausible that if thiophene and furan display similar chemisorptive behavior as benzene does, the binding energies of thiophene and furan would be larger than that of benzene. This inference is confirmed by the present B3LYP/6-31G(d) cluster model calculations. At the B3LYP/6-31G(d) level, the predicted binding energies for the [4 + 2] cycloaddition products of thiophene and furan on the Si_9H_{12} model surface are 34.3 and 30.0 kcal/mol, respectively, which are larger than that of benzene (21.8 kcal/mol predicted at the same level of theory).

Apart from the [4 + 2] and [2 + 2] products, we have also found for thiophene a S-linked physisorbed state, PS (see Figure 1d), and for furan a O-linked physisorbed state, PO (see Figure 1e). In the PS state of thiophene, the S atom of thiophene is linked with the buckled-down Si atom of the surface dimer, with a S−Si distance of 2.588 Å; the molecular plane of thiophene is tilted away from the surface normal. The binding energy is 2.9/3.3 kcal/mol with/without ZPE corrections predicted at the B3LYP/6-31G(d) level. The large S−Si separation as well as the low binding energy implies that the interaction between thiophene and the surface is primarily electrostatic, as the buckled-down Si atom of the surface dimer is positively charged. In the PO state of furan, the molecular plane of furan is coplanar with the surface dimer with its O heteroatom linked with the buckled-down Si atom of the surface dimer. The binding energy is 6.4/7.3 kcal/mol with/without ZPE corrections predicted at the B3LYP/6-31G(d) level. With a large O−Si distance (2.171 Å), the interaction between furan and the surface is mainly electrostatic. It is noteworthy that the bonding configuration of furan adsorbed in the PO state resembles one of the several bonding configurations of pyridine on the same surface site, for which a strong N−Si bond was revealed with a binding energy of 28.4 kcal/mol at the same level of theory.[43]

3.2. Isomerization and Decomposition of Chemisorbed C_4H_4X (X = S,O). We have shown that both thiophene and furan preferentially undergo [4 + 2] cycloaddition onto the dimer site of the Si(100)-2 × 1 surface using the Si_9H_{12} cluster model. On the real Si(100)-2 × 1 surface, the thus-formed di-σ bonded adspecies (LM1) may undergo either [2 + 2] cycloaddition between the rest >C=C< bond (in the adspecies) and a neighboring Si=Si site, forming a tetra-σ bonded surface species, or undergo migration of the heteroatom to a neighboring Si=Si site, resulting in a six-member ring metallocycle and adsorbed heteroatom. Hereafter, these two processes are referred to as the isomerization process and the decomposition process, respectively. We have investigated these two processes by using a double-dimer model, $Si_{15}H_{16}$. This larger model also enables us to investigate the effect of cluster size. The optimized geometries of the key points in the two reaction pathways are depicted in Figure 2. The relative energies and some selected geometrical parameters of the key points are given in Table 2 for thiophene and Table 3 for furan, respectively.

We first consider the thiophene/$Si_{15}H_{16}$ model system. The [4 + 2] cycloaddition of thiophene onto one of the dimer site of the $Si_{15}H_{16}$ cluster can lead to two products, LM1_d and LM1′_d, as shown in Figure 2,a and d, respectively. These two isomers, however, should be identical on the Si(100)-2 × 1 surface. Indeed, our B3LYP/6-31G(d) calculations predicted similar values of binding energy and geometries for the two isomers; e.g., the binding energy of 33.4 kcal/mol for LM1_d and 34.0 kcal/mol for LM1′_d. Both are in good agreement with those for LM1 obtained by using the Si_9H_{12} cluster. This indicates that the effect of cluster size is negligible from Si_9H_{12} to $Si_{15}H_{16}$.

For the isomerization process starting from LM1_d, further [2 + 2] cycloaddition of the 2,5-dihydrothiophene-like adspecies with a neighboring Si=Si site proceeds through a transition state, TS2_d (see Figure 2b). The predicted barrier height at TS2_d is 20 kcal/mol with respect to LM1_d. However, TS2_d is lower than the initial reactants (thiophene and $Si_{15}H_{16}$) by 13.4 kcal/mol, suggesting that this isomerization process can take place
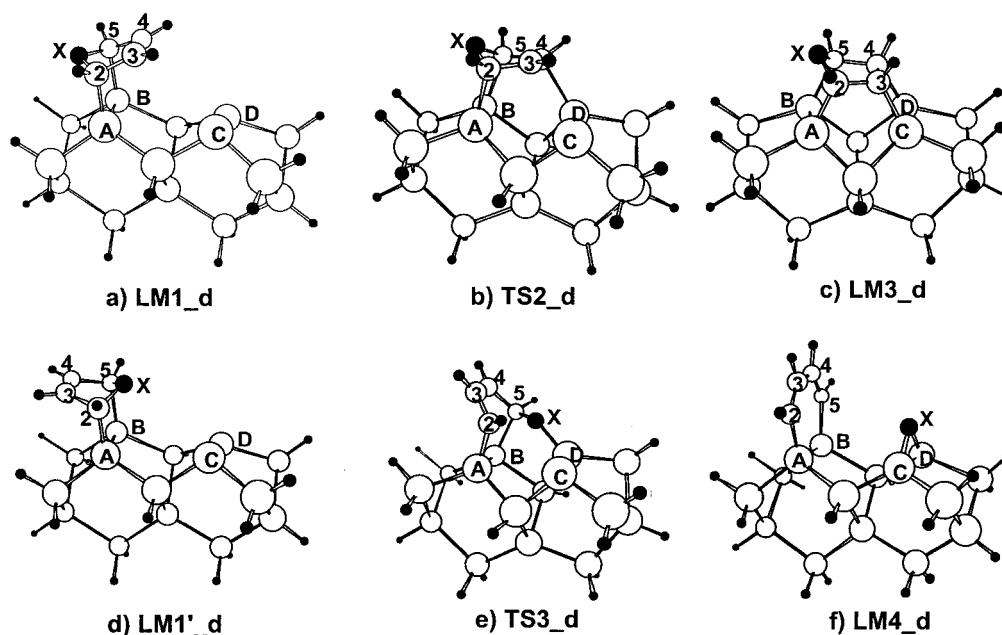
Figure 2. Local minima and transition states for the $C_4H_4X/Si_{15}H_{16}$ (X = S,O) systems predicted at the B3LYP/6-31G(d) level of theory.

TABLE 2: Adsorption Energies[a] and Selected Geometric Parameters of the Local Minima and Transition States in the C_4H_4S/ $Si_{15}H_{16}$ Model System from B3LYP/6-31G(d) Calculations

	reacts.	LM1_d	LM1′_d	TS2_d	LM3_d	TS3_d	LM4_d
$Si_A–Si_B$ (Å)	2.266	2.373	2.374	2.380	2.366	2.369	2.354
$Si_C–Si_D$ (Å)	2.266	2.249	2.252	2.416	2.342	2.428	2.324
$C_2–Si_A$ (Å)		1.967	1.967	2.020	1.954	1.899	1.875
$C_5–Si_B$ (Å)		1.964	1.965	1.945	1.954	1.948	1.875
$C_3–Si_C$ (Å)		3.954		3.123	1.985		
$C_4–Si_D$ (Å)		4.148		2.269	1.985		
$S–Si_C$ (Å)			4.091			3.597	2.192
$S–Si_D$ (Å)			4.155			2.238	2.192
$C_2–C_3$ (Å)	1.368	1.508	1.509	1.480	1.562	1.439	1.355
$C_3–C_4$ (Å)	1.430	1.342	1.342	1.404	1.596	1.361	1.471
$C_4–C_5$ (Å)	1.368	1.508	1.509	1.543	1.562	1.501	1.355
$C_2–S$ (Å)	1.735	1.860	1.858	1.869	1.861	2.772	4.504
$C_5–S$ (Å)	1.735	1.859	1.855	1.876	1.861	1.896	4.504
ΔE (kcal/mol)	0.0	−33.4	−34.0	−13.4	−52.5	−17.4	−84.0
	(0.0)	(−35.5)	(−35.1)	(−14.7)	(−55.5)	(−18.1)	(−82.0)

[a] Adsorption energy $\Delta E = E(C_4H_4S/Si_{15}H_{16}) - E(Si_{15}H_{16}) - E(C_4H_4S)$. Energies without zero-point energy corrections are given in parentheses.

TABLE 3: Adsorption Energies[a] and Selected Geometric Parameters of the Local Minima and Transition States in the C_4H_4O/ $Si_{15}H_{16}$ Model System from B3LYP/6-31G(d) Calculations

	reacts.	LM1_d	LM1′_d	TS2_d	LM3_d	TS3_d	LM4_d
$Si_A–Si_B$ (Å)	2.266	2.366	2.366	2.382	2.364	2.383	2.352
$Si_C–Si_D$ (Å)	2.266	2.249	2.249	2.417	2.344	2.371	2.295
$C_2–Si_A$ (Å)		1.995	1.994	2.078	1.982	1.929	1.875
$C_5–Si_B$ (Å)		1.992	1.992	1.958	1.982	1.980	1.875
$C_3–Si_C$ (Å)		3.968		3.128	1.973		
$C_4–Si_D$ (Å)		4.167		2.225	1.973		
$O–Si_C$ (Å)			4.035			3.277	1.739
$O–Si_D$ (Å)			4.181			1.809	1.739
$C_2–C_3$ (Å)	1.361	1.502	1.502	1.465	1.568	1.455	1.356
$C_3–C_4$ (Å)	1.436	1.342	1.342	1.412	1.592	1.346	1.471
$C_4–C_5$ (Å)	1.361	1.502	1.502	1.555	1.568	1.459	1.356
$C_2–O$ (Å)	1.364	1.442	1.443	1.434	1.440	2.120	4.463
$C_5–O$ (Å)	1.364	1.442	1.443	1.456	1.440	1.467	4.463
ΔE (kcal/mol)	0.0	−28.8	−29.0	−8.7	−48.0	−9.0	−76.2
	(0.0)	(−30.8)	(−30.8)	(−9.4)	(−51.0)	(−9.1)	(−76.9)

[a] Adsorption energy $\Delta E = E(C_4H_4O/Si_{15}H_{16}) - E(Si_{15}H_{16}) - E(C_4H_4O)$. Energies without zero-point energy corrections are given in parentheses.

at elevated temperature. In TS2_d, the forming $C_4–Si_D$ and $C_3–Si_C$ bond lengths are 3.123 and 2.269 Å, respectively, showing that this [2 + 2] cycloaddition is nonconcerted. The product, a tetra-σ bonded, tetramethylene sulfide-like surface species (LM3_d in Figure 2c) is 19.1 kcal/mol lower than LM1_d, and

its formation energy is −52.5 kcal/mol with respect to free thiophene and $Si_{15}H_{16}$. It should be mentioned that previous theoretical work[24-26] revealed the formation of a similar tetra-σ bonded adspecies for benzene chemsorbed on the Si(100)-2 × 1 surface at elevated temperatures.

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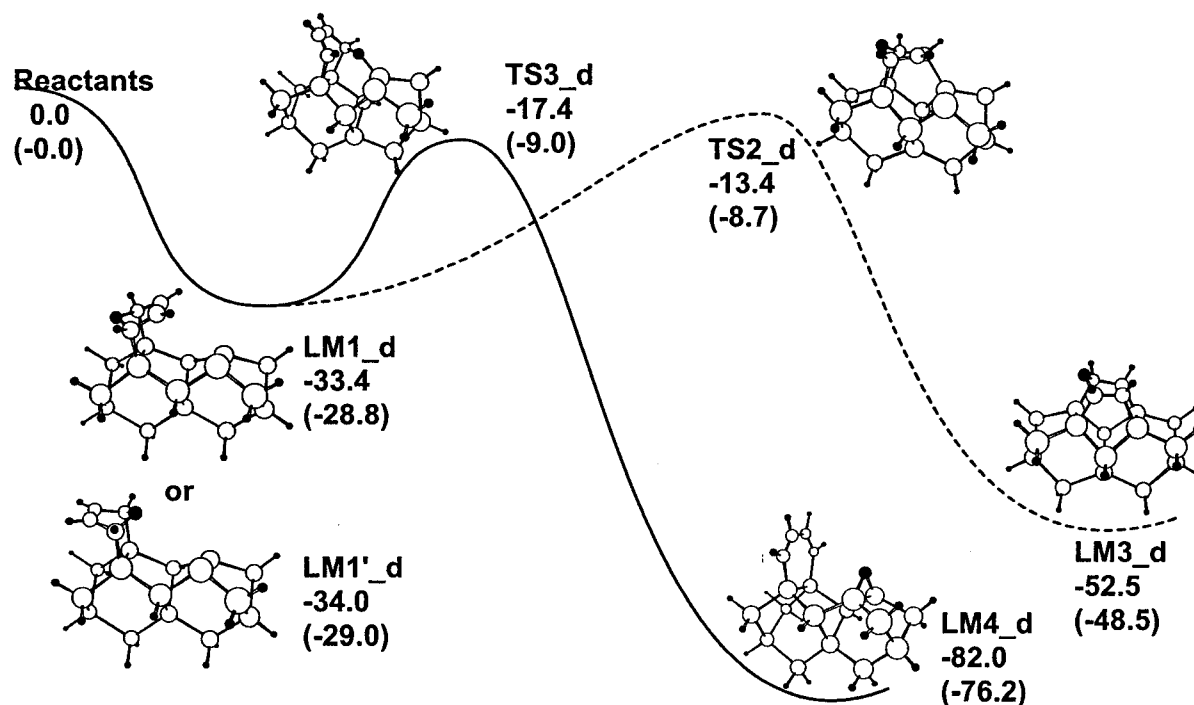
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Figure 3. Profile of energy surface (PES) for the reaction pathways of $C_4H_4X/Si_{15}H_{16}$ (X = S,O) model systems predicted at the B3LYP/6-31G(d) level of theory. For furan, energies are given in parentheses. (Units in kcal/mol)

TABLE 4: Comparison of the Calculated[a] Vibrational Frequencies (cm^{-1}) for Free Thiophene and Furan with Experiment[b]

	thiophene		furan	
modes	calc.	expt.	calc.	expt.
=C−H str.	3143, 3142, 3103, 3090	3126, 3125, 3098, 3086	3176, 3171, 3146, 3135	3161, 3154, 3149, 3129
in-plane ring	1517, 1410, 1357	1504, 1409, 1360	1549, 1468, 1375, 1127, 1030	1556, 1491, 1384, 1140, 1040
=C−H bend.	1238, 1075, 1073, 1019	1256, 1085, 1083, 1036	1247, 1174, 1056	1267, 1180, 1066

[a] Wavenumbers larger than 1000 cm^{-1} are presented here. [b] Experimental data extracted from ref 44.

For the decomposition process starting from LM1′_d, the abstraction of S atom from the 2,5-dihydrothiophene-like adspecies by a neighboring Si=Si site proceeds via a transition state, TS3_d (see Figure 2e), producing a six-member ring metallocyclic and a triangular C_2S surface species (see LM4_d in Figure 2f). The barrier height at TS3_d is predicted to be 16.6 kcal/mol with respect to LM1′_d. The transition state TS3_d is 17.4 kcal/mol lower than the initial reactants, free thiophene and $Si_{15}H_{16}$. At TS3_d, the two broken C−S bond lengths are 1.896 and 2.772 Å; the two forming Si−S bond lengths are 2.238 and 3.597 Å (cf. Table 2). In the product LM4_d, the six-member ring metallocyclic surface species has the C_2−C_3 and C_4−C_5 bond lengths of 1.355 Å, which is typical for a C=C double bond, as well as two C−Si bond lengths of 1.875 Å and a Si−Si bond length of 2.354 Å. The triangular Si_2S surface species has two S−Si bond lengths of 2.192 Å and a Si−Si bond length of 2.324 Å. This decomposition (desulfurization) process is exothermic with a reaction heat of −48 kcal/mol with respect to LM1′_d and of −82.0 kcal/mol with respect to the initial reactants, free thiophene and $Si_{15}H_{16}$. LM4_d is also 29.5 kcal/mol lower than the tetra-σ bonded, tetramethylene sulfide-like surface species produced by the isomerization process. From the predicted energetics, it can be seen that starting from the di-σ bonded, dihydrothiophene-like chemisorbed thiophene, the desulfurization process producing metallocyclic surface species and S(a) is both kinetically and thermodynamically favorable over the isomerization process that leads to the tetra-σ bonded, tetramethylene sulfide-like surface species.

In the case of furan, similar isomerization and decomposition processes have been found for the di-σ bonded, dihydrofuran-like chemisorbed furan, as shown in Figure 2 and Table 3. The results can be summarized as follows: (i) the isomerization process gives rise to a tetra-σ bonded, tetrahydrofuran-like surface species, while the decomposition (deoxygenation) process leads to a six-member ring metallocycle and an epoxy surface species; (ii) the deoxygenation process is thermodynamically favorable over the isomerization process; (iii) both processes, however, have equivalent activation energy, unlike the thiophene case, in which the decomposition process is found to be kinetically more favorable over the isomerization process. The profile of energy surface for the chemisorption, isomerization, and decomposition of thiophene and furan on the double-dimer $Si_{15}H_{16}$ cluster model is depicted in Figure 3, which schematically demonstrates their similar chemisorptive behavior on the Si(100)-2 × 1 surface.

3.3. Vibrational Frequencies of Chemisorbed C_4H_4X (X = S,O). The vibrational frequencies of the various adspecies in the $C_4H_4X/Si_{15}H_{16}$ (X = S,O) model systems have been calculated at the B3LYP/6-31G(d) level and scaled by a factor of 0.96. For free thiophene and furan, the predicted vibrational frequencies larger than 1000 cm^{-1} are presented in Table 4, along with the experimental values,[44] showing that the theoretical calculations faithfully reproduce the experimental data. In Table 5, the calculated vibrational frequencies ($>$900 cm^{-1}) for the di-σ bonded, 2,5-dihydrothiophene-like surface species are tabulated. For comparison, the experimental data[20] for the $C_4H_4S/Si(100)$ chemisorption system are also listed in Table 5.

TABLE 5: Comparison of the Calculated Vibrational Frequencies[a] (cm^{-1}) for Adspecies in the C$_4$H$_4$S/Si$_{15}$H$_{16}$ Model System with Experiment

	calc.			expt.[c]
mode	di-σ bonded (LM1_d)	tetra-σ bonded (LM3_d)	metallocycle (LM4_d [b])	120 K
=C−H str.	3100, 3081		3030, 3022, 3007, 2995	3054
−C−H str.	3019, 3017	2993, 2992, 2962, 2947		2920
C=C str.	1585		1623, 1530	
=C−H in-plane bend.	1300, 1089		1377, 1339, 1202, 1177	1180, 1088
=C−H out-of-plane bend.			991, 973	
−C−H bend.	1176, 1162, 1051, 1033	1233, 1223, 1151, 1124, 1089, 1065, 1044, 1031		
C−C str.	935, 924	938, 905		946

[a] Wavenumbers larger than 900 cm^{-1} are given here. *[b]* The frequency of the SiS stretching mode is 550 cm^{-1}. *[c]* Reference 20.

TABLE 6: Calculated Vibrational Frequencies[a] (cm^{-1}) for Adspecies in the C$_4$H$_4$O/Si$_{15}$H$_{16}$ Model System

mode	di-σ bonded (LM1_d)	tetra-σ bonded (LM3_d)	metallocycle (LM4_d)
=C−H str.	3127, 3107		3030, 3022, 3008, 2995
−C−H str.	3011, 3009	3000, 2998, 2963, 2949	
C=C str.	1573		1585, 1529
=C−H in-plane bend.	1302, 1072		1375, 1339, 1202, 1178
=C−H out-of-plane bend.			991, 974
−C−H bend.	1272, 1220, 1117, 1092	1263, 1216, 1211, 1209, 1165, 1069, 1163, 1049	
C−C str.	973, 952	947, 936	

[a] Wavenumbers larger than 900 cm^{-1} are given here. *[b]* The frequency of the SiO stretching mode is 789 cm^{-1}.

In their HREELS experiments, Qiao et al. observed several bands around 3054, 2920, 1180, 1088, and 946 cm^{-1} for sub-monolayer thiophene on the Si(100)-2 × 1 surface at 120 K, and assigned them to =C−H stretching mode, −C−H stretching mode, =C−H bending mode (two bands), and C−C stretching mode, respectively, of the di-σ bonded, 2,5-dihydrothiophene-like surface species.[20] The assignment is partially supported by our calculations. On the basis of our results, the band around 1180 cm^{-1} should be assigned to the −C−H bending mode, not to the =C−H bending mode, of the di-σ bonded, 2,5-dihydrothiophene-like surface species. The C=C bond stretching mode of the di-σ bonded, 2,5-dihydrothiophene-like surface species could not be detected by HREELS, because the C=C bond is parallel to the surface. Besides the calculated vibrational frequencies of the di-σ bonded, 2,5-dihydrothiophene-like surface species, the calculated vibrational frequencies of the tetra-σ bonded tetramethylene sulfide-like surface species and of the six-member ring metallocyclic surface species are also given in Table 5. At 700 K, Qiao et al. observed a broad band around 2948 cm^{-1} a weak band at 1014 cm^{-1} in HREELS spectra.[20] On the basis of our calculations, these bands can be assigned to the −C−H stretching mode and to the −C−H bending mode of the tetra-σ bonded, tetramethylene sulfide-like surface species, respectively. For the six-member ring metallocyclic surface species, its C=C stretching mode may be detectable by HREELS as the molecular plane is perpendicular to the Si(100) surface. We noticed that in the HREELS reported by Qiao et al., a shoulder peak at about 3100 cm^{-1} is discernible at temperatures higher than 450 K,[20] which can be assigned to the C=C stretching mode of the six-member ring metallocycle-like surface species.

The calculated vibrational frequecies for various adspecies in the C$_4$H$_4$O/Si$_{15}$H$_{16}$ model system are given in Table 6. Unfortunately, no experimental data are available for comparison. Nevertheless, the data presented in Table 6 should be informative to those who are interested in performing experimental vibrational analysis of the furan/Si(100) chemisorption system.

4. Concluding Remarks

The chemisorption and decomposition of thiophene (C$_4$H$_4$S) and furan (C$_4$H$_4$O) on the reconstructed Si(100)-2 × 1 surface have been investigated by means of hybrid density functional B3LYP method in combination with the cluster model approach. Two chemisorption mechanisms, [4 + 2] and [2 + 2] cyclo-additions of C$_4$H$_4$X (X = S,O) onto a surface dimer site, have been examined comparatively. The calculations revealed that the former process is barrierless and favorable over the latter one, which requires an activation energy of 2.6 kcal/mol for thiophene and 1.2 kcal/mol for furan. The di-σ bonded surface species formed by [4 + 2] cycloaddition-type chemisorption can either undergo further [2 + 2] cycloaddition with a neighboring Si=Si dimer site, giving rise to a tetra-σ bonded surface species, or undergo deoxygenation (desulfurization) by transferring the heteroatom to a neighboring Si=Si dimer site, leading to a six-member ring metallocyclic C$_4$H$_4$Si$_2$ surface species. The latter process is found to be slightly more favorable than the former, especially in the case of thiophene.

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