

Diels-Alder addition of some 6- and 5-member ring aromatic compounds on the Si(001)-2×1 surface: dependence of the binding energy on the resonance energy of the aromatic compounds

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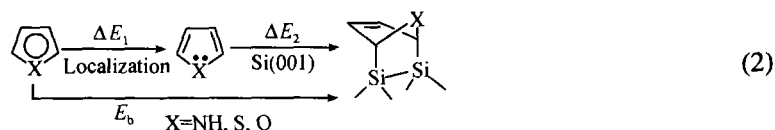
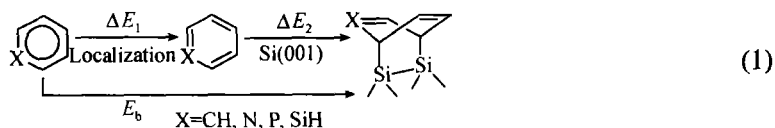
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Abstract An energy decomposition scheme is proposed for understanding of the relative low binding energy of the [4+2] cycloaddition of benzene on the Si(001)-2×1 surface. By means of density functional cluster model calculations, this scheme is demonstrated to be applicable to some other 6- and 5-member ring aromatic compounds, giving a trend that the binding energy of the [4+2] cycloaddition products of those aromatic compounds on the Si(001) surface depends strongly on their resonance energy.

Keywords: silicon, aromatic compound, adsorption, Diels-Alder reaction, cluster model, density functional theory.

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-film of conducting polymers^[1,2]. Growing efforts devoted to this topic include the experimental studies of the adsorption of benzene (C₆H₆)^[3], pyridine (C₅H₅N)^[4], furan (C₄H₄O)^[5,6], thiophene (C₄H₄S)^[5,7] and pyrrole^[5] on the Si(111) surface and the adsorption of benzene^[8-10] and pyrrole^[11] on the Si(001)-2×1 surface, as well as the theoretical studies of benzene adsorption on the Si(001)-2×1 surface^[12-15]. Of particular interest is that recent experimental and theoretical studies revealed the occurrence of [4+2] cycloaddition (Diels-Alder reaction) of benzene onto the weakly π -bonded Si-Si dimer of the Si(001)-2×1 surface and that the binding energy of the thus-formed di- σ bonded, butterfly-like adspecies is far lower than that of the analogous reaction of simple dienes (e.g., 1,3-cyclohexadiene (C₆H₈)) on the same surface^[8,12-15]. This intriguing phenomenon can be ascribed to the aromatic stabilization in benzene^[12]. For a better understanding of this intriguing phenomenon, a simple energy decomposition scheme (see scheme 1(1)), which correlates the binding energy of the [4+2] cycloaddition product with the resonance energy (E_R) of benzene, is proposed in this paper. We will show that this simple scheme is applicable to

other 6- and 5-member ring aromatic compounds and that the binding energy of the corresponding [4+2] cycloaddition products on the Si(001)-2×1 surface displays strong dependence on the resonance energy of the aromatic compounds.



Scheme 1. Energy decomposition schemes for the adsorption of 6- and 5-member ring aromatic compounds on a Si-Si dimer site of the Si(001)-2×1 surface.

1 Energy decomposition scheme

In scheme 1(1), the [4+2] cycloaddition process is divided into two ideal steps. First, the π -conjugated benzene is ideally localized into a nonaromatic analog, i.e., 1,3-cyclohexadiene. The energy cost (ΔE_1) in this step should correspond to the so-called resonance energy (E_R)^[16] of benzene. Second, the nonaromatic analog undergoes [4+2] cycloaddition onto a Si-Si dimer. This step is exothermic with a reaction heat (ΔE_2) close to the heat of the analogous reaction of 1,3-cyclohexadiene on the same surface site. Therefore, the difference in binding energy between the [4+2] cycloaddition products of benzene and 1,3-cyclohexadiene should have a value close to the difference in E_R between benzene and 1,3-cyclohexadiene. This is indeed the case, as previous B3LYP/6-31G** cluster model calculations^[12] did predict a difference of 136.3 kJ/mol in binding energy between benzene and 1,3-cyclohexadiene, which is comparable to the difference (~ 118.3 kJ/mol)^[16] in E_R between benzene and 1,3-cyclohexadiene.

Scheme 1(1) can be generalized to the cases of other 6-member ring aromatic compounds containing one (or more) heteroatom(s) and to those of the 5-member ring aromatic compounds depicted in scheme 1(2). For example, for a series of 6-member ring compounds listed in scheme 1(1), their nonaromatic analogs contain the same localized dienes as the 1,3-cyclohexadiene has and would have similar values of ΔE_2 when undergoing [4+2] addition on the Si(001) surface. Note that among them, benzene has the largest value of E_R . It is thus deducible that the [4+2] cycloaddition reactions of the heterocyclic ones would be more exothermic than that of benzene and would follow such a trend that the compound having higher E_R would give lower binding energy. A similar trend could also be expected for the 5-member ring compounds listed in scheme 1(2). To confirm the above inference, we have performed density functional cluster model calculations to explore the energetics of the [4+2] cycloaddition of five 6-member ring compounds, including benzene, pyridine, silabenzene (C_5H_6Si), phosphabenzene (C_5H_5P), pyrazine ($C_4H_4N_2$)

and 1,3-cyclohexadiene, and four 5-member ring compounds, including pyrrole, thiophene, furan and cyclopentadiene (C_5H_6), onto a Si-Si dimer site of the Si(001)- 2×1 surface.

2 Computational model and method

We used a Si_9H_{12} cluster^[12,15] to model the Si-Si dimer site on the reconstructed Si(001)- 2×1 surface. The hybrid B3LYP density functional method^[17,18] and the standard 6-31G* basis set were employed in our calculations. Adsorption geometries were optimized at the B3LYP/6-31G* level of theory with no geometric constraint. Binding energy was calculated at the same level of theory without zero-point energy (ZPE) correction. All calculations were performed using the Gaussian98 program^[19].

Table 1 Key structural and energetic parameters for the products of [4+2] cycloaddition of some 6- or 5-member ring aromatic compounds on the Si(001)- 2×1 surface (predicted at the B3LYP/6-31G* level)

	6-member ring					5-member ring				
	C_6H_6	C_5H_5P	C_5H_5N	C_5H_6Si	$C_4H_4N_2$	C_6H_8	C_4H_3N	C_4H_4S	C_4H_4O	C_5H_6
C-Si/nm	0.1976	0.1979	0.1977	0.1978	0.1965	0.1953	0.2010	0.1965	0.1993	0.1965
	0.1976	0.1954 ^{a)}	0.1973 ^{a)}	0.1958 ^{a)}	0.1965	0.1953				
Si-Si-C/(°)	96.2	97.2	95.6	98.3	94.8	96.6	89.2	92.5	88.5	90.4
	96.2	98.3 ^{a)}	95.3a)	99.9a)	94.8	96.6				
E_b /kJ \cdot mol ^{-1b)}	-91.1	-121.2	-106.6	-109.9	-123.7	-234.9	-105.3	-150.5	-128.7	-217.4
E_R /kJ \cdot mol ⁻¹¹⁶⁾	118.3	108.7	107.0	105.8	94.9	0.0	94.1	69.0	50.6	0.0
ΔE_2 /kJ \cdot mol ^{-1c)}	-209.4	-229.9	-213.6	-215.7	-218.6	-234.9	-199.4	-219.5	-179.3	-217.4

a) Parameters relevant to the carbon atom neighboring to the heteroatom; b) $E_b = E(\text{adsorbate}/C_9H_{12}) - E(\text{adsorbate}) - E(C_9H_{12})$; c) $\Delta E_2 = E_b - E_R$.

3 Results and discussion

The B3LYP-calculated key structural and energetic parameters for the [4+2] addition products of those 6- and 5-member ring compounds on the Si-Si dimer sites are listed in table 1, together with the theoretical resonance energy reported by Dewar et al.^[16] and the values of ΔE_2 estimated with the formulae $\Delta E_2 = E_b - E_R$. Our B3LYP/6-31G* calculations reveal that:

(i) The [4+2] cycloaddition process on the Si(001)- 2×1 surface is exothermic for all the 6- and 5-member ring compounds concerned. The products are di- σ bonded adspecies with the thus-formed Si-C bond lengths ranging within 0.195—0.201 nm.

(ii) The nonaromatic ones, i.e., 1,3-cyclohexadiene and cyclopentadiene, give the largest binding energy, whereas the most aromatic ones, benzene and pyrrole, give the smallest binding energy in the 6- and 5-member ring compounds, respectively.

(iii) The calculated binding energy for the 6-member ring compounds gives the following order of magnitude: C_6H_8 (-234.9 kJ/mol) > $C_4H_4N_2$ (-123.7 kJ/mol) > C_5H_5P (-121.2 kJ/mol) > C_5H_6Si (-109.9 kJ/mol) > C_5H_5N (-106.6 kJ/mol) > C_6H_6 (-91.1 kJ/mol). Taking C_5H_5P as an exception, we found that this is the reverse order of their E_R values. That is, the higher E_R the compound has, the lower the binding energy given in the Diels-Alder addition-like adsorption on

the Si(001)-2×1 surface is. A similar trend was also found for the 5-member ring compounds, and expected that the more aromatic thiophene gives larger binding energy than the less aromatic furan does.

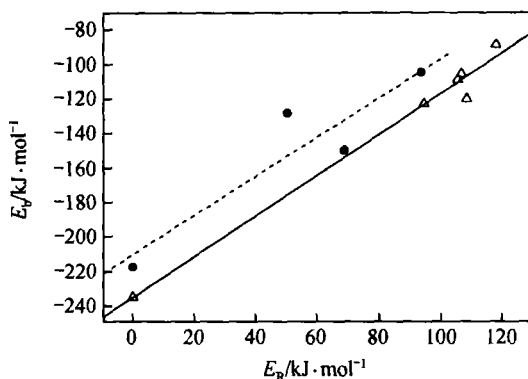


Fig. 1. Calculated binding energy (E_b) for the [4+2] cycloaddition of some 6- and 5-member ring compounds on the Si(001) surface as a function of the resonance energy (E_R) of these compounds. Further linear fitting gives the solid line and dashed line for 6- and 5-member ring compounds, respectively. Δ , 6-member ring; \bullet , 5-member ring.

and thiophene for the 5-member ring compounds might be a reflection of either the rather different ring strains of those compounds from those of other compounds of the same lines or the imperfectness of the E_R values reported^[16]. Note that the determination of E_R is a subject of long-term controversy^[16].

In summary, we have proposed an energy decomposition scheme for the understanding of the relative low binding energy of the [4+2] cycloaddition of benzene on the Si(001)-2×1 surface. By means of density functional cluster model calculations, we demonstrate that this scheme is applicable to some other 6- and 5-member ring aromatic compounds and the binding energy of the [4+2] cycloaddition products of those aromatic compounds on the Si(001) surface depends strongly on their resonance energy. We should note that other bonding configurations of those 6- and 5-member ring compounds on the Si(001)-2×1 surface, e.g., the di- σ bonding configurations involving direct heteroatom-surface bond and the tetra- σ bonding configurations, have also been considered in our calculations. The results will be published elsewhere. Needless to say, the energy decomposition scheme proposed for the Diels-Alder addition-like surface reaction is also applicable to the normal Diels-Alder reactions between aromatic compounds and alkenes.

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