

## Supporting Information

### Effects of $\beta$ C-Substituents and Terminal Unsaturated Groups on H-abstraction Reactions of Unsaturated Molecules on the H-terminated Si(100)-(2 $\times$ 1): Density Functional Theory Investigations

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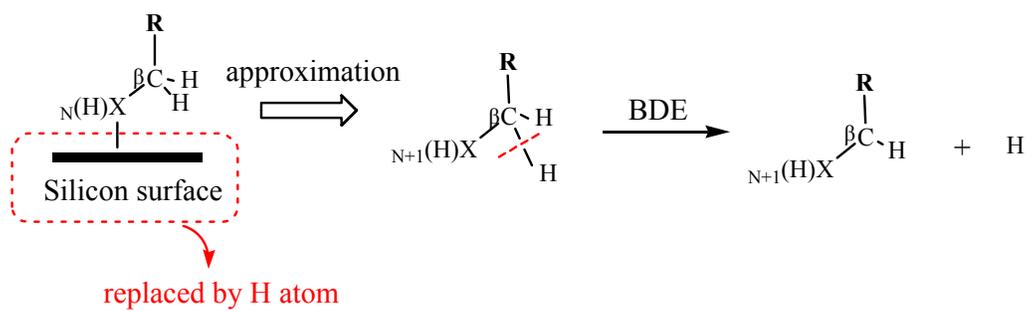
#### I. Schemes of evaluations of BDEs.

The BDEs of Si-X (X = C, N, O) bonds are evaluated qualitatively via the silane approximation. The B3LYP/6-311+G(d,p) is used in the calculation.

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	$E_{Si-X}$ (kcal/mol)	The silane approximation
<b>1</b> (Si-C(sp3))	80.82	$H_3SiCH_2-CH_2-CH_3 \rightarrow H_3Si\cdot + \cdot CH_2-CH_2-CH_3$
<b>2</b> (Si-C(sp3))	80.13	$H_3SiCH_2-CH_3 \rightarrow H_3Si\cdot + \cdot CH_2-CH_3$
<b>8</b> (Si-C(sp2))	92.24	$H_3SiCH=CH_2 \rightarrow H_3Si\cdot + \cdot CH=CH_2$
<b>10</b> (Si-O)	100.90	$H_3Si-O-CH_2-CH_3 \rightarrow H_3Si\cdot + \cdot O-CH_2-CH_3$
<b>12</b> (Si-N(sp))	78.00	$H_3Si-N=CH-CH_3 \rightarrow H_3Si\cdot + \cdot N=CH-CH_3$
<b>14</b> (Si-N(sp2))	89.98	$H_3Si-N-CH_2-CH_3 \rightarrow H_3Si\cdot + \cdot N-CH_2-CH_3$

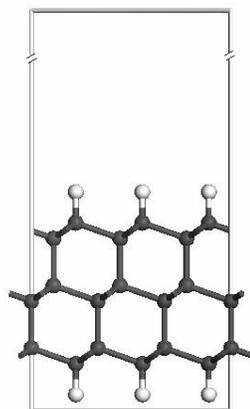
The BDEs of  $\beta$ C-H bonds are evaluated qualitatively by replacing the silicon surface with the hydrogen atom as shown below. The B3LYP/6-311+G(d,p) is used in the estimation of the BDE.



## II. Comparisons between periodic slab model and cluster model

To obtain a better understanding of factors influencing prediction of H-abstraction barriers, we further carry out periodic DFT calculations on reaction path of H-abstraction reactions of ethene and styrene molecules on the H-Si(111) in the framework of periodic slab models.

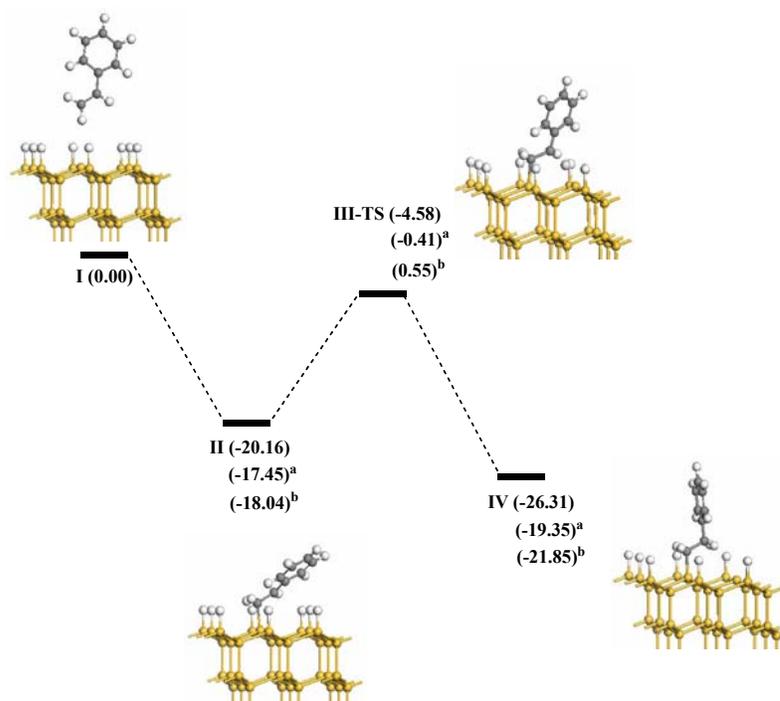
A (3×3) H-Si(111) surface cell (11.50×11.50×25.0 Å<sup>3</sup>, Fig. S1) with six layers of silicon atoms present is used to study the H-abstraction reactions of ethene and styrene. The periodic DFT calculations performed using the generalized gradient approximation (GGA) as implemented in Vienna Ab-initio Simulation Package (VASP)<sup>35</sup> with the bottom two layers of silicon atoms and the lowest layer of hydrogen atom fixed at optimized positions. The exchange-correlation functional of Perdew and Burke, and Enzerholf (PBE) is adopted.<sup>36</sup> The plane-wave basis set is used with the 310 eV cutoff, and the **k** space integration is done with the mesh of 3×3×1. The nudged elastic band (NEB) method implemented in the VASP package is used for the determination of the reaction path. The reactant, transition state, and product are confirmed by frequency calculations.



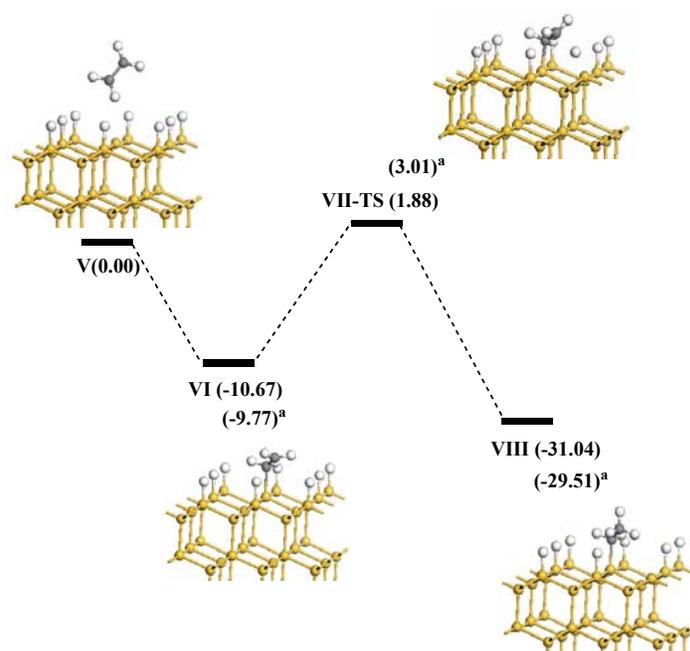
**Figure S1.** The periodic slab model of H-Si(111).

We find the energy curves predicted by the periodic slab model are in good agreement with those derived from the cluster model approximations as shown in **Fig. S2**. Moreover, the difference between optimized geometries of intermediate (**II**, **VI**), transition state (**III-TS**, **VII-TS**), and reaction product (**IV**, **VIII**) via the cluster model and the periodic slab model is very small (c.f. **Table S1**), indicating the size of surface model and exchange-correlation functional employ small influences on the prediction of reaction path of H-abstraction on the silicon surface.

On the other hand, the cluster model and the periodic slab model consistently suggest the phenyl group in the reaction product (**IV**) orients preferably vertical conformation relative to the ethyl group, differing from previous calculation results.<sup>20a,b</sup> The energy difference between the coplanar conformer and the vertically oriented conformation is predicted to be 0.96 kcal/mol (periodic model) and 1.44 kcal/mol (cluster approximation<sup>21b</sup>), respectively. In fact, the coplanar conformer is identified as a transition state structure, because an imaginary frequency is found. The Intrinsic Reaction Coordinates (IRC) calculations confirm our postulation of the transition state structure. We thus consider that the disagreement of prediction of H-abstraction barriers of styrene molecule between current work and previous reports<sup>20</sup> is most likely caused by different geometries of reaction product used in determining the reaction path, because the transition state structure and reaction barriers obtained by string method<sup>37,38</sup> and the nudged elastic band (NEB) method depend strongly on geometries of reactant and reaction product.



(a)



(b)

**Figure S2.** Energy curves of H-abstraction reaction of (a) styrene and (b) ethene molecule on the H-Si(111) studied by the periodic slab model. <sup>a</sup> The energy values are referred to [Table S1](#). <sup>b</sup> The energy values are referred to [Ref. 21b](#). The unit of energy is kcal/mol.

**Table S1.** The comparison of geometries of the intermediate (**Im**), transition state (**TS**), and reaction product (**Pr**) optimized by the periodic slab model, the cluster model, and previous theoretical results based on the periodic slab and cluster models.

<b>Geometries</b>	<b>Im</b>	<b>TS</b>	<b>Pr</b>
<i>Ethene molecule</i>			
	1.96 (1.95)	1.94 (1.94)	1.91 (1.92)
Si- $\alpha$ C (Å)	2.03 <sup>a</sup>	1.96 <sup>a</sup>	1.92 <sup>a</sup>
	1.47 (1.48)	1.49 (1.50)	1.53 (1.54)
$\alpha$ C- $\beta$ C (Å)	1.44 <sup>a</sup>	1.50 <sup>a</sup>	1.53 <sup>a</sup>
Improper dihedral angle	2.4 (5.1)	22.1 (23.3)	37.3 (37.3)
$\alpha$ C- $\beta$ H <sub>1</sub> - $\gamma$ C- $\beta$ H <sub>2</sub> (°)	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>
<i>Styrene molecule</i>			
	1.95 (1.95)	1.93 (1.93)	1.92 (1.92)
Si- $\alpha$ C (Å)	1.96 <sup>b</sup>	1.95 <sup>b</sup>	1.93 <sup>b</sup>
	1.96 <sup>a</sup>	1.93 <sup>a</sup>	1.94 <sup>a</sup>
	1.47 (1.48)	1.51 (1.52)	1.54 (1.55)
$\alpha$ C- $\beta$ C (Å)	1.49 <sup>b</sup>	1.53 <sup>b</sup>	1.54 <sup>b</sup>
	1.47 <sup>a</sup>	1.48 <sup>a</sup>	1.54 <sup>a</sup>
	1.42 (1.42)	1.45 (1.46)	1.51 (1.51)
$\beta$ C- $\gamma$ C (Å)	1.42 <sup>b</sup>	1.47 <sup>b</sup>	1.52 <sup>b</sup>
	1.41 <sup>a</sup>	1.42 <sup>a</sup>	1.53 <sup>a</sup>
Improper dihedral angle	-0.3 (-0.56)	22.9 (21.9)	35.6 (36.1)
$\alpha$ C- $\beta$ H- $\gamma$ C- $\beta$ C (°)	1.14 <sup>b</sup>	24.9 <sup>b</sup>	36.0 <sup>b</sup>
	- <sup>a</sup>	- <sup>a</sup>	- <sup>a</sup>

<sup>a</sup> Referring to Ref. 20a

<sup>b</sup> Referring to Ref. 21b

<sup>c</sup> **Values in bracket** derived from the geometries of **Im**, **TS**, **Pr** in reactions of ethene and styrene on the H-Si(100)-2 $\times$ 1.