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ccMolecular Simulation study of Alkyl Monolayers on Si(III) Surface

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Abstract: The structure of eight-carbon monolayers on the H-terminated Si(III) surface was investigated by molecular simulation method. The best substitution percent 50% for octene or octyne-derived monolayer can be obtained using molecular mechanics calculation. And the densely packed, well-ordered monolayer on Si(III) surface can be shown through energy minimization in the suitable-size simulation cell.

Keywords: Alkyl monolayer, Si(III) surface, molecular simulation.

The preparation of monolayers on silicon surface is of growing interest for potential applications in biosensor or semiconductor technology. Different experimental technique can be used to investigate the alkyl modified Si(III) surfaces[1-4], such as X-ray photoelectron spectroscopy (XPS), Fourier transform infrared absorption spectra(FTIR), scanning electron microscopy (SEM), Auger electron spectroscopy (AES), scanning tunneling microscope (STM), and so on. These experimental results can help to understand the densely packed, well-ordered monolayer on Si(III) surface. At the same time, some theoretical calculations[5-7] such as quantum mechanics and molecular mechanics methods were performed to investigate the structures on Si(III) surface. These calculations can provide the geometry of alkyl monolayer and some interesting results at the atomic level.

Recently, Cicero[8] reported the photoreactivity of H-Si(III) with dioxygen and terminally unsaturated hydrocarbons (1-octene, 1-octyne), and got the alkyl monolayer thickness and substitution percentage on Si(III) surface experimentally, but theoretical investigations about mesoscopic structure properties corresponding to Cecreo's works have not been found in the literature. In this letter, the molecular packing structures, substitution percentage and packing energies of eight-carbon adsorbates monolayer are studied using molecular simulation method.

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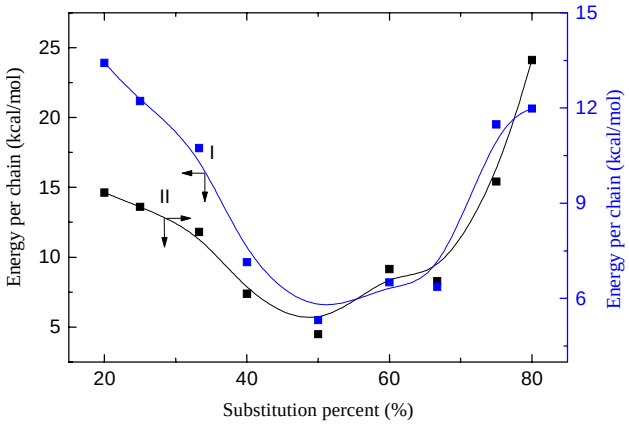
Results and Discussion

Molecular substitution percentage

All molecular mechanics calculations were performed using the MSI program Cerius2. The structures were optimized using the universal force field (UFF) and the "Smart Minimizer" with "high-convergence" criteria[5]. A 3.840Å×3.840Å×28.000Å small unit cell consists of one alkyl chain being perpendicular to the Si surface and four Si atoms that represent the atoms in four-layer Si(III) crystal. Different one-dimensional simulation cells including 1×1，1×2，1×3 and 1×4 simulation systems are designed through the unit cell repeated in *x* direction. In term of the numbers of hydrogen atoms on Si(III) surface in these one-dimensional simulation cells, different substitution percent can be obtained from 20% to 100%.

Figure 1 indicates the molecular energies per alkyl chain as a function of the molecular substitution percents. Obviously, the octene or octyne-derived monolayer at 50 substitution percent has the lowest energy, it implies that the best substitution percentage is 50 %, which is near to the experiment results 45± 3%[8].

Figure 1 The energy per alkyl chain vs substitution percent



Molecular substitution pattern

When 50% substitution is selected, there are a few substitution patterns on Si(III) surface. **Figure 2** shows the simulation cells with different substitution patterns at substitution percentage 50%. These simulation cells are obtained by repeating the unit cell in two dimensions (*x* and *y* directions). The calculated energies *per* alkyl chain for these substitution patterns are listed in **Table 1**.

As shown in **Table 1**, the energy *per* chain of pattern *i* for octene or octyne-derived monolayers is the lowest. So, substitution pattern *i* was used for further study on how molecular orientations affect the structures of octene-derived monolayers on Si(III) surface. **Table 1** also shows that the loose patterns have relatively low energies, such as patterns *d*, *e*, *g*, *i* and *k*, and the energies of the concentrated patterns such as *f* and *j* are

relatively high. These means that two or three neighboring alkyl chains are favor to the substitution on Si(III) surface. For example, patterns *i* or *g* is two or three aggregates with neighboring alkyl chain and has the relatively low energy, while pattern *j* is four aggregates with neighboring alkyl chain and has the highest energy. These phenomena indicate that not only van der Waals interactions among alkyl chains on Si(III) surface but also the steric effects of alkyl chains are important to the structures of alkyl monolayers.

Figure 2 Simulation cells of different substitution patterns at 50% substitution for octane- and octyne-derived monolayers

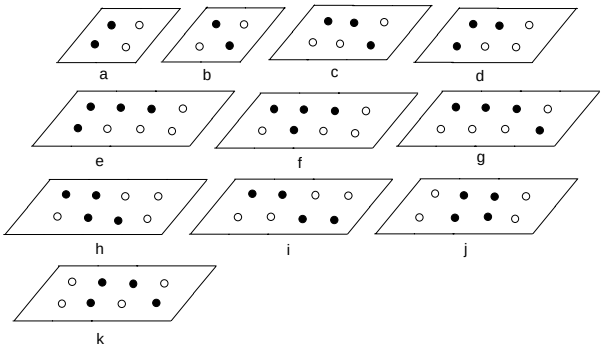


Table 1 The energies per alkyl chain for different substitution patterns at 50% substitution

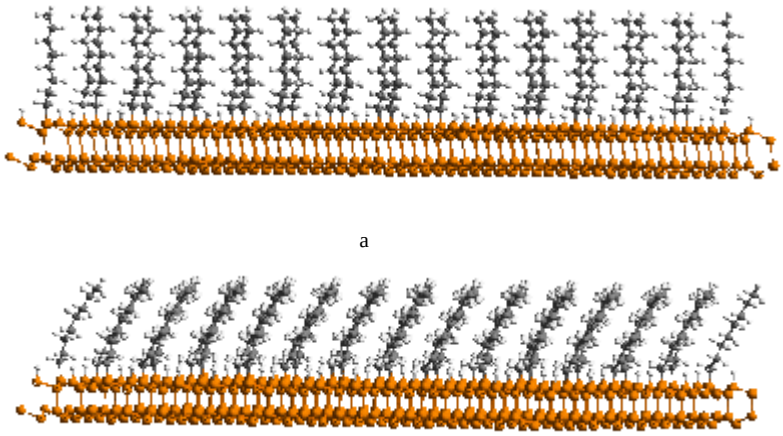
Substitution pattern	Simulation cell	Energy per chain (kcal/mol)	
		Octane-derived	octyne-derived
a	(2×2)	-4.828	-10.694
b	(2×2)	-2.568	-8.378
c	(2×3)	-1.948	-10.717
d	(2×3)	-3.412	-9.171
e	(2×4)	-3.667	-15.727
f	(2×4)	-1.546	-7.886
g	(2×4)	-10.329	-19.243
h	(2×4)	-2.783	-6.476
i	(2×4)	-12.301	-20.857
j	(2×4)	1.568	12.339
k	(2×4)	-11.643	-8.7409

Alkyl chain geometry on Si(111) surface

After substitution pattern *i* is selected, some different simulation cells can be obtained *via* (2×4) unit cell of pattern *i* repeated in *x* and *y* direction. Before optimized, the input geometry in (8×16) simulation cell contains 32 hydrogen atoms and 32 alkyl chain being perpendicular to the first layer Si(III) surface (**Figure 3a**). After optimized using molecular mechanics calculation, all the alkyl chains tilt to the Si surface (**Figure 3b**). The tilt angle is around 10 degree and the calculated thickness of the monolayer is 10.8±

0.2 Å. It is in good agreement with 9±2 Å in the literature[8].

Figure 3 Alkyl monolayer on Si(III) surface before and after optimization



a

b

a and b, the side view of the input and optimized geometry of (8×8) simulate cell

From the discussion above, the simulation result such as substitution percentage and title angel of alkyl chain is in good agreement with the experiments. So, one conclusion is shown that molecular simulation can show the geometry alkyl monolayer on Si(III) surface, and provide otherwise inaccessible mesoscopic information. The molecular simulation can be considered as an adjunct to experiments.

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