Adsorption Behaviors of Chlorosilanes, HCl, and H₂ on the Si(100) Surface: A First-Principles Study

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ABSTRACT: The hydrochlorination process is a necessary technological step for the production of polycrystalline silicon using the Siemens method. In this work, the adsorption behaviors of silicon tetrachloride (SiCl₄), silicon dichloride (SiCl₂), dichlorosilane (Si₂H₂Cl₂), trichlorosilane (SiHCl₃), HCl, and H₂ on the Si(100) surface were investigated by first-principles calculations. The different adsorption sites and adsorption orientations were taken into account. The adsorption energy, charge transfer, and electronic properties of different adsorption systems were systematically analyzed. The results show that all of the molecules undergo dissociative chemisorption at appropriate adsorption sites, and SiHCl₃ has the largest adsorption strength. The analysis of charge transfer indicates that all of the adsorbed molecules behave as electron acceptors. Furthermore, strong interactions can be found between gas molecules and the Si(100) surface as proved by the analysis of electronic properties. In addition, SiCl₄ can be formed by the dissociation of SiCl₆, SiH₃Cl₂, and SiHCl₃. The transformation process from SiCl₄ to SiCl₂ is exothermic without any energy barrier. While SiH₂Cl₂ and SiHCl₃ can be spontaneously dissociated into SiHCl₂, SiHCl₃ should overcome about 110 kJ/mol energy barrier to form SiCl₄. Our works can provide theoretical guidance for hydrochlorination of SiCl₄ in the experimental method.

1. INTRODUCTION

Polycrystalline silicon has been regarded as the critical raw material for solar cell manufacturing, and the Siemens process is widely used to produce polycrystalline silicon. However, the entire process produces large amounts of silicon tetrachloride (SiCl₄) and HCl as byproducts. By employing hydrogenation technology, this excess SiCl₄ can be converted back into useful trichlorosilane (SiHCl₃), which is the starting material for chemical vapor deposition of polycrystalline silicon. In general, there are two hydrogenation routes, namely, thermal hydrogenation and hydrochlorination. The first route involves the hydrogenation of SiCl₄ at a high temperature (>1373 K). The overall reaction is

\[ \text{SiCl}_4(g) + H_2(g) \rightarrow \text{SiHCl}_3(g) + \text{HCl}(g) \]  

(1)

The second one is known as hydrochlorination, which has a lower energy consumption and higher conversion in comparison with thermal hydrogenation. The reacting system is as follows

\[ 3\text{SiCl}_4(g) + \text{Si(s)} + H_2(g) \rightarrow 4\text{SiHCl}_3(g) + \text{HCl}(g) \]  

(2)

However, the hydrochlorination of SiCl₄ is relatively complex, and there are some intermediate products generated during the formation of SiHCl₃, such as SiCl₂, SiH₂Cl₂, and so on. There is still no consensus about the complex reactions which can occur, especially concerning the gas–silicon surface interactions. Currently, the first-principles calculations can effectively reveal the microcosmic interactions of the gas–silicon surface.

The Si(100) surface is proved to be very stable because of the low surface energy, and it undergoes reconstruction after full relaxation, i.e., the undercoordinated surface Si atom pair usually results in the formation of dimers. Therefore, the interactions between the active silicon surface and gas molecules have received extensive investigations. For instance, Hall et al. used the density functional theory (DFT) method to study the adsorption behaviors of chlorosilanes (SiH₂Cl₂, SiHCl₃, and SiCl₄) on the Si(100) surface and found that the scission of SiH₂Cl₂ and SiHCl₃ is more inclined to pass through the Si–Cl bond instead of the Si–H bond. Ng et al. employed the DFT computation to investigate the micro-

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Figure 1. (a) Nine atomic layers of the Si(100) structure and (b) side view and (c) top view of seven atomic layers of the Si(100) structure, and different adsorption styles for the SiCl₄ molecule: (d) hole site, (e) top site, and (f) bridge site.

cosmic mechanism for disilane (Si₂H₄) adsorption on Si(100). They found that Si₂H₄ is dissociative adsorbed on the Si(100) surface, and the Si–H bonds are more prone to rupture compared with Si–Si bonds. Besides, some interesting phenomena can be observed after single-molecule adsorption on Si(100). For example, the SiCl₂, SiCl₃, and SiCl₄ clusters can be formed after the Si atom is adsorbed on the chlorinated Si(100) surface. When the Cl atom is adsorbed on the Si(100) surface under ultrahigh vacuum conditions, the dissociated Cl and the active Cl radicals can lead to the formation of SiCl₂. Additionally, in contrast with the dissociative adsorption suggested by some available kinetic models, Anzai et al. indicated that SiCl₄ undergoes molecular adsorption at the Si(100) surface. However, the fundamental understanding of the adsorption and reaction mechanism of byproducts generated by the Siemens process (including chlorosilanes, HCl, and H₂) on the Si(100) surface are still lacking, which is difficult to be studied by the traditional experimental method.

Therefore, the first-principles calculations were adopted to simulate the adsorption behaviors of chlorosilanes (SiCl₄, SiCl₂, SiH₂Cl₄, and SiHCl₃), H₂, and HCl on the Si(100) surface in this work, which aims to reveal the gas–silicon surface interactions in the hydrochlorination process of SiCl₄. The adsorption energy, charge transfer, and electronic properties, including total charge density (TCD), charge density difference (CDD), and density of states (DOS) of the gas–silicon surface, were also revealed. The results of this study help to provide a theoretical basis for exploring the reaction mechanism and experimental work of the hydrochlorination of SiCl₄.

2. CALCULATION METHODS AND MODELS

2.1. Calculation Method. In this work, the Dmol³ package with the dual numerical plus polarization (DNP) basis set was used to perform all of the DFT calculations. To treat the electron change and correlation interactions, the Perdew–Burke–Ernzerhof (PBE) form of the generalized gradient approximation (GGA) functional was selected. Specifically, the Brillouin zone integrations were performed using a Monkhorst–Pack grid of 6 × 6 × 1 k points, and all calculations were nonspin polarized. We chose the 4.6 Å cutoff radius for geometry optimization, where a smearing value of 0.005 Ha was employed for rapid convergence. Effective core potential (ECP) of the Hartree–Fock potential is used to treat inner electrons. When the force of relaxed atoms is lower than 5 × 10⁻⁵ Ha, the force change between two steps is smaller than 0.02 Ha/Å, and the atomic structures tend to be stable. To avoid the interaction of each layer during the calculations, a vacuum layer thickness of 15 Å was added to the top of the Si(100) surface. The adsorption energy (E_ads) is calculated as follows:

\[ E_{ads} = E_{gas/Si(100)} - E_{gas} - E_{Si(100)} \]  

where \( E_{gas/Si(100)} \) is the total energy of Si(100) with gas adsorption and \( E_{gas} \) and \( E_{Si(100)} \) are the total energies of the isolated gas molecule and Si(100) surface, respectively.

The charge density difference (\( \Delta \rho \)) is calculated using the following expression:

\[ \Delta \rho = \rho_{gas/Si(100)} - \rho_{gas} - \rho_{Si(100)} \]

where \( \rho_{gas/Si(100)} \), \( \rho_{gas} \), and \( \rho_{Si(100)} \) are the charge density of gas adsorbed on the Si(100) surface, free gas molecule, and Si(100) surface, respectively.

2.2. Surface Model. Silicon (Si) has a diamond-like and tetrahedral structure, and the optimized lattice parameter (5.470 Å) and bulk modulus (91.1 GPa) in this work are consistent with the experimental result (5.500 Å and 97.8 GPa). The adsorption energies of SiCl₄ on seven and nine atomic layers (Figure 1a,b) at the top site were calculated. Both cases belong to dissociative adsorption (SiCl₂⁺ Cl⁻), and the slab with seven atomic layers is large enough. Thus, to improve the calculated efficiency, seven atomic layers of Si(100) were selected in this work. Si(100) is modeled with p(3×3) supercells with seven atomic layers, and the surface energy is calculated to be 153 mJ/m², which is also close to the theoretical values of 100–200 mJ/m². Our calculation results are in good agreement with the experimental and theoretical values, which verifies the accuracy of this calculation. The bottom layer was passivated with two hydrogen atoms per silicon atom, as shown in Figure 1a. During the calculation process, the bottom two layer atoms are fixed, and the other layer atoms and adsorbed molecules are relaxed. Figure 1 shows the Si(100) surface structure, which contains the three dimers, and the middle dimer is selected as the adsorption site. To determine the most stable structure of gas molecules on Si(100), four possible adsorption
sites are considered, including top1 (top of Si3), top2 (top of Si4), bridge (bridge site of the Si3−Si4 bond), and hole (central site of the middle dimer) sites, as shown in Figure 1b, and the four Si atoms in the first layer are marked with “Si1”, “Si2”, “Si3”, and “Si4”, respectively. Taking the SiCl4 molecule as an example, the adsorption styles of gas molecules are plotted in Figure 1d–f.

3. RESULTS AND DISCUSSION

3.1. Stability and Geometric Structures. First, we calculate the adsorption energy of gas molecules on the Si(100) surface at different adsorption sites, as listed in Table 1. One can see that SiCl4, SiCl2, SiH2Cl2, SiHCl3, HCl, and H2 molecules are spontaneously dissociated into a single atom (H and Cl) after full relaxation, and the decomposed H and Cl atoms bond with Si atoms of Si(100).

The charge transfer (ΔQ) can be employed to evaluate the interaction strength between gas molecules and the Si(100) surface, and it should be pointed out that the negative (positive) value means the gas molecule gains (loses) electrons. The charge transfer number for adsorption systems is correlated with different adsorption sites. Table 1 gives out the calculated ΔQ of the most stable adsorption systems based on the Hirshfeld charge. One can see that the electrons transferred from the Si(100) surface to SiCl4, SiCl2, SiH2Cl2, SiHCl3, HCl, and H2 molecules are 0.241, 0.061, 0.109, 0.288, 0.214, and 0.136 e, respectively. This outcome indicates that all of the gas molecules behave as electron acceptors, while the Si(100) surfaces act as electron donors. From Table 1, the SiHCl3 gas molecule obtains the maximum electrons and thus exhibits the largest adsorption strength, which agrees well with the above results of Eads.

Table 1. Adsorption Energies and Corresponding Adsorption Products on Different Adsorption Sites of the Si(100) Surface

| molecule | adsorption site | reaction products | Eads (eV) |
|----------|----------------|--------------------|-----------|
| SiCl4    | top1           | SiCl4* + Cl*       | −1.57     |
|          | top2           | SiCl4* + Cl*       | −1.73     |
|          | bridge         | SiCl2* + 2Cl*      | −2.46     |
|          | hole           | SiCl* + 3Cl*       | −1.99     |
| SiCl2    | top1           | SiCl*              | −1.88     |
|          | top2           | SiCl*              | −2.18     |
|          | bridge         | SiCl*              | −2.06     |
|          | hole           | SiCl* + Cl*        | −2.17     |
| SiH2Cl2  | top1           | SiH2Cl* + Cl*      | −1.47     |
|          | top2           | SiH2Cl*            | −0.18     |
|          | bridge         | SiHCl*             | −0.19     |
|          | hole           | SiHCl* + H*        | −1.86     |
| SiHCl3   | top1           | SiHCl3* + Cl*      | −1.96     |
|          | top2           | SiHCl3* + Cl*      | −1.91     |
|          | bridge         | SiHCl3* + Cl*      | −1.82     |
|          | hole           | SiHCl* + 2Cl*      | −2.63     |
| HCl      | top1           | H* + Cl*           | −2.60     |
|          | top2           | HCl*               | −0.10     |
|          | bridge         | HCl*               | −0.11     |
|          | hole           | H* + Cl*           | −2.59     |
| H2       | top1           | H2*                | −0.08     |
|          | top2           | H2*                | −0.09     |
|          | bridge         | 2H*                | −1.96     |
|          | hole           | H2*                | −0.09     |

“Here, * denotes a surface site.”

molecules are preferentially adsorbed at the bridge, top2, hole, hole, top1, and bridge sites with the Eads of −2.46, −2.18, −1.86, −2.63, −2.60, and −1.96 eV, respectively. Moreover, the adsorption strength of SiHCl3 is larger than those of the other gas molecules (SiCl4, SiCl2, SiH2Cl2, SiHCl3, HCl, and H2) due to the higher adsorption energy.

Figure 2 gives the most stable configurations of SiCl4, SiCl2, SiH2Cl2, SiHCl3, HCl, and H2 adsorbed on the Si(100) surface. We can find that most of the molecules are dissociative adsorption on Si(100) except for the SiCl4 molecule, and all of the gas molecules strongly interact with the Si(100) surface by a chemical bond. This outcome indicates that those adsorption processes belong to chemisorption. The SiCl4 molecule can be spontaneously dissociated into SiCl3 and Cl atoms as plotted in Figure 2a. The bond length of Si−Cl1 and Si−Cl4 is stretched from 2.043 Å (experimental result is 2.090 Å) to 5.177 and 3.906 Å, respectively. For the SiCl4 molecule, it is vertically adsorbed on the surface, and the Si atom of SiCl4 bonds with two nearest-neighbor Si atoms of the Si(100) surface, which matches well with the results obtained by Anzai.22 In addition, the SiH2Cl2 molecule spontaneously dissociates into SiHCl2 and one H atom, while the SiHCl3 molecule dissociates into SiHCl and two Cl atoms, as shown in Figure 2a, b, and c. Also, the HCl and H2 molecules are spontaneously dissociated into a single atom (H and Cl) after full relaxation, and the decomposed H and Cl atoms bond with Si atoms of Si(100).

3.2. Adsorption of Chlorsilane Molecules on the Si(100) Surface. To further understand the microcosmic interactions of the gas−silicon surface, the total charge density (TCD) and charge density difference (CDD) of the SiCl4−Si(100) adsorption system were calculated and are shown in Figure 3. The strong overlapping of TCD can be found between SiCl4 and the Si(100) surface (shown in Figure 3a), which indicates that the SiCl4 molecule strongly interacts with the Si(100) surface. Moreover, from Figure 3b, there are large blue regions around SiCl4, which indicates that a large number of electrons are transferred from the Si(100) surface to SiCl4. Thus, the SiCl4 molecule acts as an electron acceptor, which agrees well with the results of Hirshfeld charge analysis.

Figure 4 displays the total density of states (TDOS) of the SiCl4−Si(100) adsorption system. As presented in Figure 4, the TDOS curve shifts to the left as a whole after SiCl4 adsorption, resulting in a decrease of total electron energy and making the electron more localized. After adsorption, the TDOS of SiCl4 shifts to lower energy and the peaks become broader and lower, making the electron more delocalized. Moreover, the number of peaks is reduced after SiCl4 adsorption, and the adsorbed SiCl4 molecule saturates the Si atoms of the Si(100) surface, which indicates that the SiCl4 molecule can be stably adsorbed on the Si(100) surface. As shown in Figure 4, the orbital hybridizations between SiCl4 and Si(100) mainly occur in the range of −12.50 to 0 eV (the green slash box area), and two resonance peaks can be observed at about −15.60 and 1.88 eV (the blue dashed outline), leading to the strong interaction between SiCl4 and the Si(100) surface. Also, there are small peaks in the range of −17 to −15 eV (the red shaded area), and these peaks are contributed from SiCl4.

The partial density of states (PDOS) of the SiCl4−Si(100) adsorption system is plotted in Figure 5. In Figure 5a, there is a resonance peak at −15.6 eV (the blue shaded area), which illustrates that the dissociated Cl1 atom from SiCl4 strongly interacts with the Si1 atom of the Si(100) surface. Meanwhile, it can be seen that there is an obvious electron orbital overlap...
between the p orbital of the Cl1 atom and s, p orbitals of the Si1 atom in the energy range of −7.5 to 0 eV (the violet slash

Figure 2. Top view (a1–a6) and side view (b1–b6) of the lowest-energy structures of different gas molecules absorbed on the Si(100) surface. The unit of bond length is Å.

Table 2. Charge Number (ΔQ, e) Transferred from the Si(100) Surface to Different Molecules for the Most Stable Adsorption Systems

| molecule | adsorption site | reaction products | ΔQ (e) |
|----------|----------------|------------------|--------|
| SiCl₄    | bridge         | SiCl₂⁺ + 2Cl⁻     | −2.46  |
| SiCl₂    | top2           | SiCl₂⁺           | −2.18  |
| SiH₂Cl₂  | hole           | SiHCl₂⁺ + H⁺      | −1.86  |
| SiHCl₃   | hole           | SiHCl⁺ + 2Cl⁺     | −2.63  |
| HCl      | top1           | H⁺ + Cl⁺          | −2.60  |
| H₂       | bridge         | 2H⁺              | −1.96  |

*Here, * denotes a surface site.

Figure 3. (a) Total charge densities (TCD) and (b) charge density differences (CDD) of SiCl₄ adsorbed on the Si(100) surface. The green represents charge, and the blue (yellow) areas are electron aggregation (depletion). The isosurface values of TCD and CDD are 0.2 and ±0.02 e/Å³, respectively.
box area), which also indicates that there are strong hybridizations among these atomic orbitals.

For SiCl\(_2\), two different adsorption styles are considered. The first one is the SiCl\(_2\) molecule adsorbed on the top2 site of the Si(100) surface vertically. There is an obvious charge overlap between the SiCl\(_2\) molecules and Si(100) (Figure 6a), namely, the SiCl\(_2\) molecule interacts strongly with Si(100).

From the CDD (Figure 6b), we can find that significant charge accumulation occurs around the SiCl\(_2\) molecule, indicating that extremely strong covalent bonds are formed on the surface; thus, SiCl\(_2\) acts as an electron acceptor. The results of PDOS (Figure 6d) show that there exist three resonance peaks at about \(-8.76\), \(-1.70\), and 1.24 eV (the shaded blue part) between Si atoms of the SiCl\(_2\) molecule and Si1 atoms of the Si(100) surface, which suggests that the strong interaction of Si–Si takes place. The other one is the SiCl\(_2\) molecule adsorbed on the Si(100) surface in a parallel manner (Figure 6c), and its \(E_{\text{ads}}\) is calculated to be \(-1.80\) eV. It should be noted that the SiCl\(_2\) molecule undergoes dissociative chemisorption, and the Si–Cl bonds of the SiCl\(_2\) molecule are stretched from 2.109 to 2.292 and 2.507 Å, respectively.

Nevertheless, from the view of adsorption energy, the vertical adsorption style of SiCl\(_2\) is much more stable.

When SiH\(_2\)Cl\(_2\) is adsorbed on the Si(100) surface, the charge of SiH\(_2\)Cl\(_2\) overlaps with the charge of Si(100) (Figure 7a), indicating that the SiH\(_2\)Cl\(_2\) molecule interacts with the Si(100) surface. The CDD (Figure 7b) shows that the electron accumulation is mainly localized on the SiH\(_2\)Cl\(_2\) molecule, manifesting the electron-withdrawing property of SiH\(_2\)Cl\(_2\). As displayed in Figure 7c, the H\(_2\)-s orbital is greatly hybrid with Si4-s,p orbitals ranging from \(-9.50\) to 0 eV (the violet slash box area), which indicates that the interactions between SiH\(_2\)Cl\(_2\) and the Si(100) surface are strong.

In Figure 8a, there are charge exchanges and overlaps between SiHCl\(_3\) and the Si(100) surface, indicating that the SiHCl\(_3\) molecule strongly interacts with the Si(100) surface. The electron density around the adsorbed SiHCl\(_3\) is significantly increased, as proved by the CDD in Figure 8b, and this suggests that many electrons of Si(100) are transferred to SiHCl\(_3\). Additionally, the strong charge transfer indicates the bonding effect. The results of PDOS (Figure 8d) show that there exist two strong resonance peaks (the blue shaded part) at \(-15.60\) eV between Cl3-s and Si4-s orbitals and at \(-3.28\) eV between Cl3-p and Si4-s,p orbitals, respectively, resulting in the strong interaction between SiHCl\(_3\) and the Si(100) surface.

Based on the above results, both SiH\(_2\)Cl\(_2\) and SiHCl\(_3\) are strongly adsorbed on the Si(100) surface at the hole site, and the adsorption strength of SiHCl\(_3\) is larger than that of SiH\(_2\)Cl\(_2\). Moreover, SiH\(_2\)Cl\(_2\) is chemically dissociated into the H atom and SiHCl\(_2\) molecule, and SiHCl\(_3\) can dissociate into the SiHCl\(_2\) molecule and Cl atom after adsorption (Figure 8c). The corresponding adsorption energy is calculated to be \(-1.82\) eV. When SiHCl\(_3\) is adsorbed at the
Figure 7. (a) TCD and (b) CDD of SiHCl$_3$ adsorbed on the Si(100) surface. (c) PDOS of H$_2$ atoms of SiHCl$_3$ and Si$_4$ atoms of the Si(100) surface. The green areas in panel (a) represent the charge density, and the blue (yellow) areas in panel (b) represent electron aggregation (depletion). The vertical black dashed line represents the Fermi level. The isosurface values of TCD and CDD are 0.2 and ±0.02 e/Å, respectively.

Figure 8. (a) TCD and (b) CDD of SiHCl$_3$ adsorbed on the Si(100) surface. (c) Top view of the optimized SiHCl$_3$–Si(100) structure at the bridge site. (d) PDOS of Cl$_4$ atoms of SiHCl$_3$ and Si$_4$ atoms of the Si(100) surface. The green areas in panel (a) represent the charge density, the blue (yellow) areas in panel (b) represent electron aggregation (depletion). The vertical black dashed line represents the Fermi level. The unit of bond length is Å. The isosurface values of TCD and CDD are 0.2 and ±0.02 e/Å, respectively.

bridge site, one of the Si–Cl bonds in the SiHCl$_3$ molecule is stretched from 2.052 to 3.979 Å. It is worth noting that the calculated adsorption behavior of a single H atom and Cl atom on the hole site of the Si(100) surface is shown in Figure 9. These two atoms are bonding with the Si(100) surface, and the corresponding adsorption energies are calculated to be −3.82 and −4.21 eV, respectively. The Si(100) surface has a larger affinity with SiHCl$_3$ in comparison with SiHCl$_2$, and this difference may be due to the fact that the adsorption capacity of a single Cl atom is stronger than that of the H atom on the Si(100) surface.

3.3. Adsorption of HCl and H$_2$ Molecules on the Si(100) Surface. From the TCD in Figure 10a, one can see that the charge overlaps between HCl and the Si(100) surface, which means that strong covalent bonds are formed between HCl and the Si(100) surface. Hou et al.$^{45}$ found that HCl was dissociative adsorbed on the Si(100) surface and H and Cl atoms adhered to the Si(100) surface, which is consistent with our conclusions in this work. From the CDD (Figure 10b), the HCl molecule is electron-rich, which indicates that the loss charges of the Si(100) surface are transferred to the HCl molecule. The results of PDOS (Figure 10c) show that the hybridizations between the Cl-s and Si4-s,p orbitals are found from −9.50 to −3.70 eV (the violet slash box area) in the valence band, and one strong resonance peak can also be observed at −3 eV (the blue shaded part), which indicates that the covalent bonding is formed between HCl and the Si(100) surface.

From the TCD in Figure 11a, the charge of the H$_2$ molecule overlaps that of the Si(100) surface when H$_2$ is adsorbed on the Si(100) surface, which indicates that there is an interaction between the H$_2$ molecule and the Si(100) surface. From the CDD (Figure 11b), one can see that the H$_2$ molecule adheres to the Si(100) surface after adsorption, which agrees well with the experimental observation by Dürr.$^{37}$ Additionally, the results of charge transfer indicate that the H$_2$ molecule acts as an electron acceptor, while the Si(100) surface acts as an electron donor. As shown in Figure 11c, the orbital hybridizations between the H$_2$ molecule and Si(100) surface mainly occur in the range of −9.50 to −1.25 eV (the violet slash box area), meaning that the H$_2$ molecule interacts strongly with the Si(100) surface.

Both the HCl and H$_2$ molecules undergo dissociative chemisorption. For HCl, the most stable adsorption site is the top1 site and the $E_{ads}$ is −2.60 eV; both H and Cl atoms form stable chemical bonds with the Si(100) surface. For H$_2$, the most stable adsorption site is the bridge site and the $E_{ads}$ is −1.96 eV; H atoms form stable chemical bonds with the Si(100) surface. Moreover, the H$_2$ adsorbed on other sites (top and hole sites) belongs to physical adsorption; thus, the adsorption of H$_2$ is more inclined to adsorb on the bridge site instead of the top and hole sites. These results suggest that Si(100) has a stronger adsorption ability for HCl in comparison with H$_2$. This difference could be due to the smaller radius of the H atom in comparison to the Cl atom, leading to the weaker interaction with surrounding Si surface atoms. Furthermore, the sticking coefficient of H$_2$ on silicon surfaces is extremely small.$^{47}$

3.4. SiCl$_2$ Formation and SiHCl$_3$ Formation Mechanism. It is known that SiCl$_2$ is an essential intermediate product for the production of polysilicon by the Siemens process,$^{48}$ which can promote the formation of SiHCl$_3$. Yadav$^{49}$ studied that the formation of SiCl$_2$ may arise from the
Si atoms of Si(100) and Cl atoms. There are three ways to form SiCl$_2$, that is, the SiCl$_4$/SiH$_2$Cl$_2$/SiHCl$_3$ molecule dissociates into SiCl$_2$. Our results show that SiCl$_4$, SiH$_2$Cl$_2$, and SiHCl$_3$ undergo dissociative chemisorption after they are adsorbed on the Si(100) surface. Moreover, the SiCl$_4$ adsorption leads to the formation of SiCl$_2$ (Figure 12a), which indicates that the SiCl$_2$ molecule is spontaneously formed during SiCl$_4$ adsorption. Specifically, the minimum energy path (MEP) to search for the involved transition state in SiCl$_4$ formation was obtained by LST/QST tools$^{34,50}$ in DMol$^3$ code 8.0. The barrier energy $E_a$ reported herein was calculated as follows

$$E_a = E_{TS} - E_{IS}$$

where $E_{IS}$ and $E_{TS}$ represent the total energy of the initial state (IS) and transition state (TS), respectively.

For SiH$_4$Cl$_2$ and SiHCl$_3$, they are only spontaneously dissociated into SiHCl$_3$ after adsorptions on the Si(100) surface, as illustrated in Figure 12b,c, whereas SiHCl$_4$ is hardly further dissociated on the Si(100) surface. Therefore, the transition of SiHCl$_3$ to SiCl$_2$ should overcome a certain energy barrier. As shown in Figure 13, the reaction of SiHCl$_3$ to SiCl$_2$ on Si(111) is exothermic with an energy of 44.38 kJ/mol, and the calculated reaction barrier is about 110.00 kJ/mol, which is smaller than that of SiHCl$_2$ dissociating into SiCl$_2$ on the Si(111) surface (147.90 kJ/mol).$^{34}$ In conclusion, SiCl$_4$ can be directly dissociated into SiCl$_2$ on the Si(100) surface. By contrast, SiH$_2$Cl$_2$ and SiHCl$_3$ molecules first dissociate into SiHCl$_2$ without zero energy barrier, and then, the SiHCl$_2$ molecule converted into SiCl$_2$ needs to overcome an energy barrier of 110.00 kJ/mol. Thus, SiCl$_4$ is more beneficial to
promote the formation of SiCl$_2$ compared with SiHCl$_3$ and SiH$_2$Cl$_2$ molecules.

The primary purpose of the hydrochlorination process is to convert SiCl$_4$ to SiHCl$_3$. However, it is difficult to convert all SiCl$_4$ to SiHCl$_3$ directly. SiCl$_3$ is a major intermediate in the hydrochlorination process, which is favorable to the formation of SiHCl$_3$. Hence, SiCl$_2$ is a prime candidate and can react with the surface-adsorbed Cl and H atoms to produce SiHCl$_3$. The H and Cl required for SiCl$_2$ and SiHCl$_3$ would be supplied from HCl dissociative adsorption. Therefore, a possible reaction mechanism is proposed through the following basic processes

$$\text{SiCl}_4(\text{g}) \rightarrow \text{SiCl}_2^* + 2\text{Cl}^* \quad (6)$$

$$\text{HCl}(\text{g}) \rightarrow \text{Cl}^* + \text{H}^* \quad (7)$$

$$\text{SiCl}_2^* + \text{H}^* + \text{Cl}^* \rightarrow \text{SiHCl}_3(\text{g}) \quad (8)$$

4. CONCLUSIONS

First-principles calculations were employed to investigate the adsorption behaviors of silicon tetrachloride (SiCl$_4$), silicon dichloride (SiCl$_2$), dichlorosilane (SiH$_2$Cl$_2$), trichlorosilane (SiHCl$_3$), HCl, and H$_2$ molecules on the Si(100) surface, and the electronic properties of different adsorption systems were analyzed. The results show that all of the gas molecules can bond with the Si(100) surface and even undergo dissociative chemisorption, and SiHCl$_3$ has stronger adsorption strength compared with the other molecules. Hirshfeld charge analysis reveals that all of the adsorbed molecules on the Si(100) surface behave as electron acceptors. Moreover, strong interactions can be found between gas molecules and the Si(100) surface as proved by the analysis of TCD, CDD, and DOS. Additionally, SiCl$_2$ can be formed by SiCl$_4$ with zero barrier paths. However, SiH$_2$Cl$_2$ and SiHCl$_3$ can be spontaneously dissociated into SiHCl$_2^*$, and then, the intermediate product SiHCl$_2^*$ needs to overcome an energy barrier of 110 kJ/mol to produce SiCl$_2$. Our results can provide a necessary theoretical basis for the reaction mechanism and experimental work of silicon tetrachloride hydrochlorination.

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Notes
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