

Adsorption Mechanisms of NH₃ on Chlorinated Si(100)-2 × 1 Surface[†]

Hee Soon Lee and Cheol Ho Choi*

Department of Chemistry, College of Natural Sciences, Kyungpook National University, Taegu 702-701, Korea

*E-mail: cchoi@knu.ac.kr

Received August 29, 2011, Accepted November 10, 2011

The potential energy surfaces of ammonia molecule adsorptions on the symmetrically chlorinated Si(100)-2 × 1 surface were explored with SIMOMM:MP2/6-31G(d). It was found that the initial nucleophilic attack by ammonia nitrogen to the surface Si forms a S_N2 type transition state, which eventually leads to an HCl molecular desorption. The second ammonia molecule adsorption requires much less reaction barrier, which can be rationalized by the surface cooperative effect. In general, it was shown that the surface Si-Cl bonds can be easily subjected to the substitution reactions by ammonia molecules yielding symmetric surface Si-NH₂ bonds, which can be a good initial template for subsequent surface chemical modifications. The ammonia adsorptions are in general more facile than the corresponding water adsorption, since ammonia is better nucleophile.

Key Words : SIMOMM, Mechanism, Ammonia, Silicon surface, *Ab initio*

Introductions

The organic molecule adsorptions on silicon surface have attracted a great deal of attentions due to its potential applications in the semiconductor industry.¹ Nitrogen-containing molecules are of interest, since it is a good electron donor. In particular, adsorption reactions of ammonia (NH₃) on Si surface have been one of the most studied reactions.

Extensive theoretical and experimental studies^{2,3} have consistently suggested that NH₃ initially adsorbs molecularly on the “down” atom of the presumed buckled silicon dimer with no activation barrier. Dissociation of the molecularly adsorbed NH₃ to form NH₂ and H proceeds with low activation energy, about 5 kcal/mol below the separated NH₃(g) and bare Si(100)-2 × 1 energy, indicating that N-H activation is extremely facile. Cao and Hamers⁴ suggested that molecularly adsorbed NH₃ yields the ‘dative bond’, which is highly ionic due to the unique geometric structures present on silicon surfaces permitting “down” atoms to act as excellent electron acceptors. The dative bond on Si(100)-2 × 1 surface is formed by donating the nitrogen lone pair electrons to one of the Si atoms. Initial molecular adsorption makes the bucking of the surface Si dimer more noticeable. As a result, a partially positive charge builds up on the electron donor nitrogen atom, while the “up” atom of the dimer builds up negative electron density, yielding a zwitterionic configuration. To account for the basic nature of negatively charged “up” atom, the notion of ‘proton affinity’ on semiconductor surface was proposed⁵ and later elaborated.⁶ Accordingly, the difference in chemical reactivity of the Ge(100)-2 × 1 and Si(100)-2 × 1 in N-H bond activation is explained as the proton affinity difference of the “up” atom towards the hydrogen of N-H bond.

Chlorine adsorption itself on the Si(100)-2 × 1 surface has been studied extensively.^{7,8} It is known that Cl₂ adsorbs dissociatively on the surface and forms a strong polar bond with Si without disrupting the 2 × 1 periodicity. Although a number of reports have attempted to determine the structure of the Cl-covered surface, however, two different surface model structures have been co-existed. The traditional model constitutes two chlorine atoms bonded to the dimer dangling bonds, making a symmetric structure,⁷ while the new proposal suggested that only single chlorine is bonded to the one of the Si atom of surface dimer, making an asymmetric structure.⁸ However, recent photoemission experiments concluded that the experimental results are more consistent with the symmetric model.⁹ In general, the chlorinated Si(100)-2 × 1 surface is less reactive, since the surface dimers are saturated with Si-Cl bonds. Therefore, it is interesting to see how the chemical adsorptions on such passivated surface are affected by the chlorinations.

The water molecule adsorption on chlorinated Si(100) surface was studied in our earlier paper.¹⁰ We showed that the water adsorptions on chlorinated surfaces are slower as compared to the bare surface. However, waters can adsorb to the surface eventually making fully Si-OH saturated surfaces. Due to the highly electronegative chlorine atoms on Si surface, the water adsorption was strongly altered as compared to those on bare Si surface.

In this paper, as an extension of our previous studies on water, potential energy surface studies of ammonia adsorption mechanisms on chlorinated surface are performed adopting the symmetric model of chlorinated Si(100)-2 × 1 surface as a starting template. Since the ammonia nitrogen is better electron donor than water oxygen, the surface reaction characters of ammonia as compared to water are the main focus of current paper. By studying the factors that govern the reactivity of various surface reactions, one hopes to gain control over these reactions to an extent that eventually leads

[†]This paper is to commemorate Professor Kook Joe Shin's honourable retirement.

to a technique to tailor the reaction characteristics.

Computational Details

The all-electron 6-31G(d)¹¹ basis set was used throughout this work. Minimum energy reaction paths were determined by first optimizing the geometries of the minima and transition states. Then, each stationary point was characterized by computing and diagonalizing the Hessian matrix (matrix of energy second derivatives). Minima (first order saddle points) are characterized by Hessians with zero (one) negative eigenvalues. In order to follow the minimum energy path (MEP), also called the intrinsic reaction coordinate (IRC) the Gonzalez-Schlegel second-order method¹² was used with a step size of 0.3 amu^{1/2}-bohr.

For the study of ammonia adsorption on chlorinated surface, MP2 single reference method was used. The GAMESS (General atomic and molecular electronic structure system)¹³ program was used for all of the computations.

In order to study surface size-effects, a hybrid quantum mechanics/molecular mechanics (QM/MM) method called SIMOMM¹⁴ (surface integrated molecular orbital molecular mechanics) was used.¹⁵ This approach embeds a smaller QM cluster in a much larger MM cluster in order to reduce or eliminate possible edge effects on the (localized) chemistry that occurs on the surface. The SIMOMM models for one and two ammonia adsorptions are composed of Cl₂NSi₉H₁₅ and Cl₂N₂Si₉H₁₈ quantum regions embedded in Cl₂NSi₄₈H₃₉ and Cl₂N₂Si₄₈H₄₂ clusters, respectively. MM3¹⁶ parameters were used for the molecular mechanics optimization part of the computations. All of the computations were done without imposing symmetry unless otherwise specified.

Results and Discussions

Single Ammonia Molecule Adsorption on Chlorinated Surface. The potential energy surface of a single ammonia adsorption pathway was explored with SIMOMM:MP2/6-

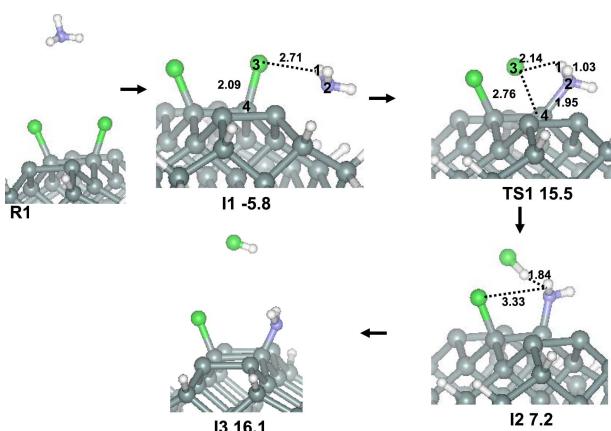


Figure 1. Structural data of initial reactant, intermediate, transition states and final product of one ammonia adsorption on chlorinated Si(100)-2 x 1 surface in Angstrom along with MP2 relative energies in kcal/mol.

31G(d) and the results are presented in Figure 1. The reference reactant, **R1** is the symmetrically chlorinated surface and NH₃. The intermediate **I1** is initially formed without an intervening reaction barrier. **I1** is stabilized by 5.8 kcal/mol as compared to **R1**, due to the weak interaction between the H1 and the electronegative Cl3. Another possible configuration of a weak interaction between N2 and Cl3 was not found. Due to the electronegativity of Cl, it is expected that the surface dimer is positively charged providing a good environment for the nucleophilic substitution by the incoming N2.

TS1 connects the **I1** and another intermediate **I2**, in which N2 is nucleophilically attacking the surface Si4, while Cl3 becomes a leaving group with the reaction barrier of 21.3 kcal/mol, which is 15.5 kcal/mol above the energy of **R1**. The reaction barrier of **TS1** is much lower than the corresponding initial water adsorption on the same surface.¹⁰ This can be due to the better electron donor of nitrogen atom of ammonia, which allows better nucleophilic attack to the Si4. Therefore, the initial ammonia adsorption reaction on chlorinated surface is expected to occur easily. Since the leaving group Cl3 is still attached to Si4 in **TS1**, it can be best viewed as a S_N2 type reaction. A unique feature of the current pathway is that the leaving Cl3 is also abstracting H1. Therefore, while the Cl3 is leaving the surface, it is also acting as a base forming a unique four-membered ring structure (H1-N2-Si4-Cl3) in **TS1**. The H1 of the leaving HCl group forms a hydrogen bond with the N2 of the surface amine group in the intermediate **I2**. The distance of H1-N2 is calculated to be 1.842 Å showing a strong bonding interaction. Other than the additional 8.9 kcal/mol endothermicity, the HCl in **I2** barrierlessly desorbs the surface yielding the final product **I3**. The reaction is overall 16.1 kcal/mol endothermic. As compared to the corresponding reaction of water adsorptions,¹⁰ overall endothermicity of **I3** is higher by 11.8 kcal/mol. Therefore, the desorption of HCl from ammonia adsorption is less facile than that of water. Overall, the ammonia can better adsorb to the chlorinated surface than water. However, the resulted HCl is more strongly trapped by the surface in the case of ammonia adorption.

Ring Closing Reaction of the Mixed Surface. The surface S_N2 reaction by a ammonia molecule yields mixed Si-Cl and Si-NH₂ on the surface dimer as shown in **R2** (see Figure 2). The N2 of the amine group has lone pair electrons that can act as a nucleophile to the electron deficient Si4. Therefore, the ring closing reaction can occur. **TS2** connecting **R2** and the ring-closed intermediate **I4** was located with the forward reaction barrier of 64.8 kcal/mol effectively prohibiting thermal ring-closing reaction. As in **TS1**, the S_N2 reaction and the hydrogen abstraction by leaving Cl occur at the same time. The HCl molecule is still making a hydrogen bond with the surface nitrogen in the intermediate **I4**, which is less stable than the reactant **R2** by 55.7 kcal/mol. Therefore, **I4** is kinetically hardly accessible and thermodynamically very unstable, which is due in part to the large ring strain of triangular configurations amine in **I4**. The desorption of the attached HCl in the **I4** requires 9.3 kcal/mol. The final product, **I5** is 65.0 kcal/mol above the energy

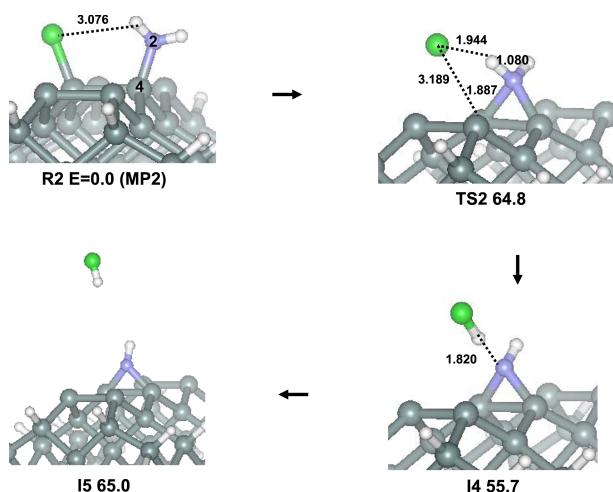


Figure 2. Structural data of initial reactant, intermediate, transition states and final product of ring-closing reaction on chlorinated Si(100)-2 × 1 surface in Angstrom along with MP2 relative energies in kcal/mol.

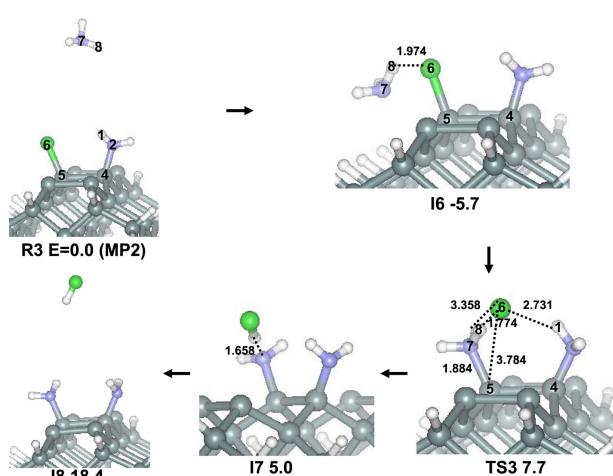


Figure 3. Structural data of initial reactant, intermediate, transition states and final product of the second ammonia adsorption on chlorinated Si(100)-2 × 1 surface in Angstrom along with MP2 relative energies in kcal/mol.

of **R2**. Consequently, ring closing reaction is not likely to occur, which was also seen in the corresponding water adsorption study.¹⁰

The Second Ammonia Molecule Adsorption. As the ammonia adsorption proceeds, more than one ammonia molecule can adsorb on the surface dimer. The first ammonia molecule adsorbed surface has both Si-Cl and Si-NH₂ as shown in **R3**. (see Figure 3) Our potential energy surface study of the second ammonia adsorption yielded the initial intermediate **I6** without a reaction barrier, which is more stable than **R3** by 5.7 kcal/mol. In **I6** intermediates, the N7 of the incoming ammonia is hydrogen-bonded to the surface Cl6. The nucleophilic attack of N6 to the surface Si5 initiates the adsorption reaction as seen in the **TS3**. At the same time, Si5-Cl6 bond is being broken and the H8-Cl6 bond is being made. The reaction barrier of **TS3** as measured from **I6** is 7.9 kcal/mol, which is 7.9 kcal/mol lower than

the initial first ammonia adsorption barrier of **TS1**. The reduced barrier height of **TS3** can be attributed to the additional hydrogen bond of Cl6-H1, which stabilizes the transition state **TS3**. The additional hydrogen bond can only be possible by the cooperative first adsorption of ammonia. The **TS3** connects the initial intermediate **I6** and di-Si-N configuration of **I7**. The leaving HCl is trapped through the H8-N7 hydrogen bond in **I7**. With additional 14.4 kcal/mol of endothermic energy, the HCl can desorb the surface. In short, current channel has a much lower reaction barrier as compared to the first ammonia adsorption due to the surface cooperative effects. Therefore, once the initial ammonia molecule adsorption occurs, the subsequent ammonia adsorptions would occur relatively easily. These two ammonia molecule adsorptions yielded amine group-only terminated surface dimer, which can provide an excellent reaction environment for the subsequent surface chemical modifications.

Conclusions

The potential energy surfaces of one and two ammonia molecule sequential adsorptions on the symmetric chlorinated surface were theoretically explored with SIMOMM:MP2/6-31G(d). One ammonia adsorption on the chlorinated surface dimer requires 15.5 kcal/mol overall reaction energy. According to our reaction mechanism studies, the lone pair electrons of incoming ammonia molecule nucleophilically attack the surface Si atom to which the Cl is bonded yielding a S_N2 type transition state. At the same time, the Cl abstracts the H atom of incoming ammonia molecule forming a unique four-membered ring conformation. Subsequent ring closing reaction of the one ammonia adsorbed surface would not easily occur due to the high reaction barrier. The second ammonia adsorption on the one ammonia adsorbed surface dimer has the overall reaction energies of 7.2 kcal/mol. It is much lower than that of the first ammonia adsorption. The reductions of the reaction barriers were attributed to the cooperative effect of already adsorbed surface species through the hydrogen-bonding.

In general, it is expected that the Si-Cl bonds of the chlorinated surface can be replaced by amine group, which is a good initial template for the subsequent surface chemical modifications. Side reactions such as surface ring closing reaction would not easily occur due to its large reaction barriers. As a first step toward establishing techniques to control the surface chemical reactions, the chlorinated surface provides promising new testing grounds.

Acknowledgments. This work was supported by National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2011-0001213 and No. 2011-0005032).

References

- Choi, C. H.; Gordon, M. S. *Theoretical Studies of Silicon Surface Reactions with Main Group Adsorbates*; Curtiss, L. A., Gordon,

- M. S., Eds., Kluwer Academic Publishers: Ch. 4, 2004; 125-190.
2. Avouris, P.; Wolkow, R. *Phys. Rev. B* **1989**, *39*, 5091.
 3. Queeney, K. T.; Chabal, Y. J.; Raghavachari, K. *Phys. Rev. Lett.* **2001**, *86*, 1046.
 4. Cao, X.; Hamers, R. J. *J. Am. Chem. Soc.* **2001**, *123*, 10988.
 5. Mui, C.; Wang, G. T.; Bent, S. F.; Musgrave, C. B. *J. Chem. Phys.* **2001**, *114*, 10170.
 6. Mui, C.; Han, J. H.; Wang, G. T.; Musgrave, C. B.; Bent, S. F. *J. Am. Chem. Soc.* **2002**, *124*, 4027.
 7. Nakayama, K.; Aldao, C. M.; Weaver, J. H. *Phys. Rev. Lett.* **1999**, *82*, 568.
 8. Martin-Gago, J. A.; Roman, E.; Refolio, M. C.; Rubio, J. M.; Lopez-Sancho, J.; Hellner, L.; Comtet, G. *Surf. Sci.* **1999**, *424*, 82.
 9. Pi, T. W.; Tsai, S. F.; Ouyang, C. P.; Wen, J. F.; Wu, R. T. *Surf. Sci.* **2001**, *488*, 387.
 10. Lee, H. S.; An, K.-S.; Kim, Y. S.; Choi, C. H. *J. Phys. Chem. B* **2005**, *109*, 10909.
 11. Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257.
 12. Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1991**, *95*, 5853.
 13. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A., Jr. *J. Comp. Chem.* **1993**, *14*, 1347.
 14. Shoemaker, J. R.; Burgraff, L. W.; Gordon, M. S. *J. Phys. Chem. A* **1999**, *103*, 3245.
 15. Cho, J.; Choi, C. H. *J. Chem. Phys.* **2011**, *134*, 194701.
 16. Allinger, N. L.; Yuh, Y. H.; Lii, J. H. *J. Amer. Chem. Soc.* **1989**, *111*, 8551.
-