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The adsorption and dissociation of ammonia on the Si₁₀ cluster surface

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Abstract. The nature of NH₃ molecule adsorption and dissociation on the Si₁₀ cluster surface has been studied by the DV-X_α method. Two isomers of Si₁₀ are considered. The calculated results show that there are different bond characters between T_d Si₁₀ and C_{3v} Si₁₀. We also present possible dissociation paths and their energy barriers for the adsorbed NH₃ molecule, and confirm the view that NH₃ cannot dissociate on either T_d Si₁₀ or C_{3v} Si₁₀ surfaces.

1. Introduction

The interaction of ammonia with Si clusters is of considerable interest, not only from the scientific viewpoint but also for the technological application of silicon nitride. Using Fourier transform ion cyclotron resonance (FTICR) with the cluster ions injected from an external laser vaporization source, Smalley and co-workers [1–4] have described studies of the reactions of silicon cluster ions with ammonia. Jarrold and co-workers [5, 6] also have studied the reaction between silicon cluster ions and ammonia using injected ion drift tube techniques and low-energy ion beam techniques. Both their results show that the reactivity of silicon cluster ions in the range of two to seventy atoms is very different from that of solid silicon. (For a review we refer to the paper of Jarrold [7].)

A number of experimental studies have been performed on the adsorption of ammonia on Si(100)-2 × 1 and Si(111)-7 × 7 surfaces [8–18]. The results show the dissociative adsorption of ammonia. Bozso and Avouris [8] have shown that a clean Si(100)-2 × 1 surface can dissociate ammonia even at temperatures as low as 90 K. On the Si(111)-7 × 7 surface, George and co-workers [9] found products of H₂ at 800 K and Si₂N at 1350 K. By theoretical analysis, we [19] studied the nature of the ammonia adsorption processes on Si(100)-2 × 1 and Si(111) (unreconstructed) surfaces. Our results show that NH₃ adsorbs dissociatively to the Si(100)-2 × 1 surface dangling bond as NH₂+H without an activation barrier. Later experimental valence band spectra by Dufour and co-workers [10] are in excellent agreement with our calculated results.

In comparison, silicon cluster ions chemisorb ammonia without dissociation. Ray and Jarrold [5] have observed that thermally activated desorption of ammonia occurs from the

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products at temperatures around 400 K. This suggests that dissociative chemisorption may well not be occurring on most of the silicon cluster ions. Also in the measurements of Jarrold's group [6], the binding energies of ammonia with silicon cluster ions range from ~ 1.3 to ~ 0.75 eV and appear to show an overall drop with increasing cluster size. If dissociative chemisorption occurred the binding energy of ammonia to the clusters would be ~ 3 eV. Thus it appears that, unlike the bulk surface, close to room temperature the reaction between the silicon cluster ions and ammonia results in molecular adsorption and not dissociative chemisorption. The large reactivity difference is surprising since the small and medium clusters consist almost only of surface atoms which are formally not saturated and therefore possess also numerous dangling bonds at the surface.

Theoretical papers on the reactivity of silicon clusters are scarce. Krack and Jug [20] have studied the adsorption of ammonia with neutral Si_5 and Si_{10} clusters using the semiempirical molecular orbital (MO) method SINDO1 and the *ab initio* program Gaussian 90. They presented the interpretation of reactivity and selectivity of ammonia with Si clusters. However, only some special adsorption sites are studied, and they did not discuss why silicon clusters chemisorb ammonia without dissociation.

The Si atoms in Si clusters are three coordinated, four coordinated, or even six coordinated, and are greatly different from those of bulk Si. The bonding characters of Si clusters are very complicated, and so far we still know very little about these. Patterson and Messmer [21] have provided some analyses of the bonding using the *ab initio* generalized valence bond approach. However the knowledge is still insufficient.

In this paper we shall study the adsorption of ammonia on the natural Si_{10} cluster surface using the DV- X_α method. Although most experimental data are obtained with ammonia adsorbed on ionic silicon clusters, it is appropriate to discuss the results for the neutral cluster which is, in many cases, more scientifically interesting in terms of the different behaviour of clusters and extended surfaces. (In any case, the calculations of Krack and Jug [20] are performed for neutral silicon clusters, and we will perform transition-state calculations for ionic clusters in the near future.) Two isomers of Si_{10} are considered. A series of possible adsorption sites is studied as well as the atop sites, and some adsorption kinetics will be presented. We also study the possible paths of ammonia dissociation, and try to interpret the different reactivity of ammonia for the bulk surface and cluster surface.

2. Models and methods

The two lowest-energy structures for the Si_{10} cluster, determined from the theoretical calculations, are shown in figure 1. They are called the tetracapped octahedron (T_d) and tetracapped trigonal prism (C_{3v}). These structures are sufficiently close in energy in the theoretical calculations that it is not possible to say with complete confidence which is the most stable. According to the experiment results of Jarrold's group, both structures probably exist [7]. Thus we consider these two isomers in our calculation.

The discrete variational X_α (DV- X_α) method, which has been described elsewhere [22–25], is employed in our calculations to develop a deeper insight into the bonding mechanism and electronic properties. The molecular wave functions and eigenvalues were determined using the self-consistent charge (SCC) approximation to the potential. In the present procedure, the Si 1s–2p and the N 1s core orbitals have not been varied, that is to say the 'frozen-core' approximation has been used.

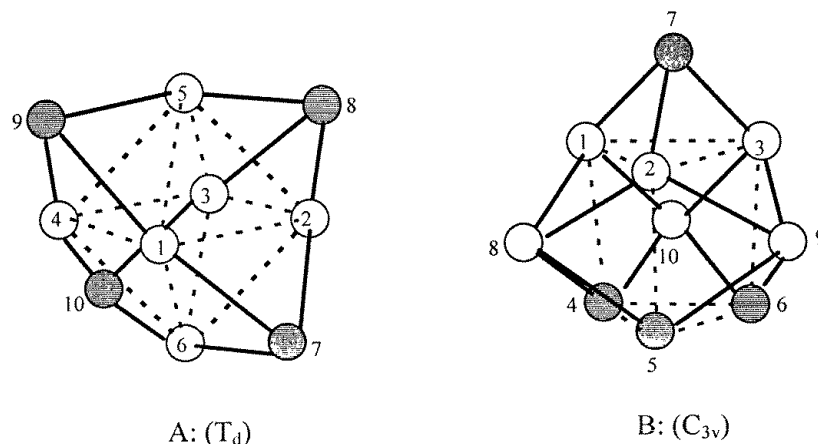


Figure 1. Two isomers of Si₁₀: (A) tetracapped octahedron (T_d), (1–6) for Si(A) and (7–10) for Si(B); (B) tetracapped trigonal prism (C_{3v}), (1–3) for Si(A), (4–6) for Si(B), (7) for Si(C), and (8–10) for Si(D).

3. Results and discussion

3.1. Adsorption of ammonia on the tetracapped octahedron (T_d) isomer surface

First, we investigate the adsorption of ammonia in the case of the tetracapped octahedron (T_d) isomer of Si₁₀. There are two kinds of atom in T_d Si₁₀ (figure 1). Atoms 1–6 (named Si(A), octahedron atoms) have six neighbour atoms and atoms 7–10 (named Si(B), cap atoms) only have three neighbour atoms. It seems that they have different bonding structure, so first we try the atop site adsorption for Si(A) and Si(B). The total energies of NH₃–Si₁₀ have been calculated at various adsorption heights, and the curves are shown in figure 2. Here we have assumed the total energy at infinite adsorption height to be zero. Figure 2 shows that Si(B) is slightly favoured over Si(A), and the adsorption energies are 0.52 and 0.30 eV for balance heights 5.02 and 5.63 au, respectively. (Here the balance height is the lowest-total-energy adsorption height.) This is reasonable because Si(B) has fewer neighbour atoms than Si(A). These results are also compatible with those available in [20] (0.73 and 0.61 eV).

For deeper understanding, we calculated the adsorption energies for some other possible sites. Figure 3 shows the adsorption energies and the balance heights for a series of sites. The reaction coordinate is from atom 5 through atom 9 and atom 4 to atom 6. In particular, in parts (b) and (d) of figure 3 the reaction coordinate is the rotation angle for atom 9 and bridge 1–4. The range of angle of rotation is from the symmetrical axis of ammonia perpendicular to the first surface to that perpendicular to the second surface.

Figure 3 shows that the most favoured adsorption site (best site) is at the top of atom 9, where the symmetrical axis of ammonia is perpendicular to the surface 1–4–9, compared to the atop site above. The adsorption energy is 1.15 eV. At the same time, there are two other equivalent sites near atom 9 (Si(B)) because of the symmetry. In order to seek the properties of the bonding character between adsorbates and atom 9, we performed calculations on the Si₁₀H₃ system in which the three H atoms are placed on the best sites near one Si(B) atom. The total binding energy is 6.17 eV for three H atoms, i.e. 2.06 eV for each H atom, and the H–Si bond length is 3.19 au. This is compatible with the 3.10 eV and 2.80 au for

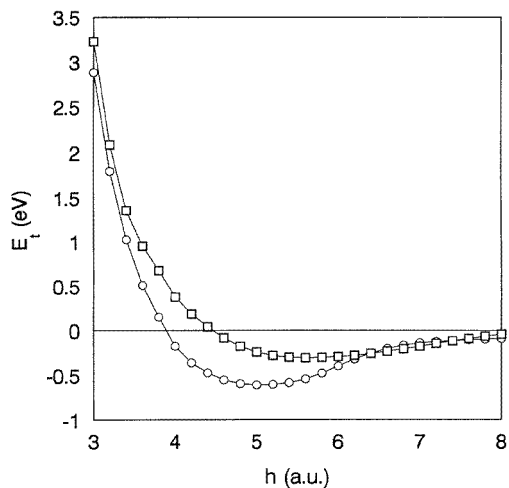


Figure 2. The total energy of the T_d Si_{10} - NH_3 cluster versus the N-Si distance h : \square , Si(A); \circ , Si(B).

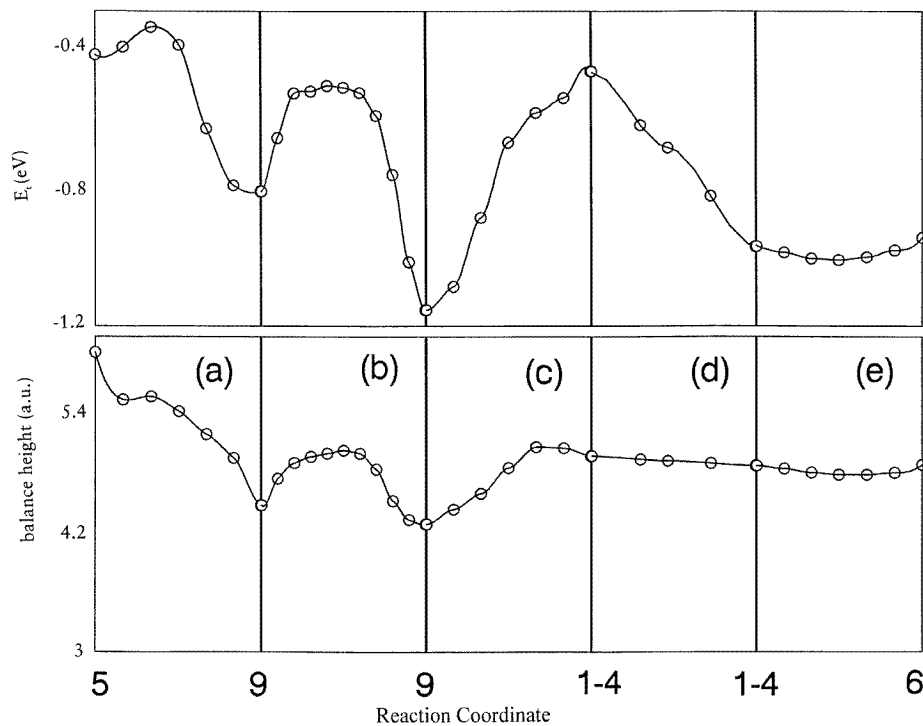


Figure 3. The adsorption energy and balance height of the T_d Si_{10} - NH_3 cluster versus the reaction coordinate for (a) moving from atom 5 to 9, (b) rotating atop of atom 9, (c) moving from atom 9 to bridge 1-4, (d) rotating atop of bridge 1-4, and (e) moving from bridge 1-4 to atom 6.

Si–H on the Si(111) surface [26]. However, the H–Si–H angle is 107.2°, and it is in good agreement with the theoretical predictions, 1.09.5° for standard sp³ hybridization. On the other hand, the bond angle of atom 1–9–4 is 65.1° for T_d Si₁₀, and this is not comparable with the 109.5° of standard sp³ hybridization. The above analyses show that there are three dangling bonds near the Si(B) and only one sp³ hybridization orbital contributes to the bond between an Si(A) atom and three Si(B) atoms, i.e. this kind of bond is a many-centre bond. On the other hand, the hexacoordinated bond structure of Si(A) atoms also shows they have a many-centre bond structure. We can find similar results of many-centre bonds in the theoretical analysis of Patterson and Messmer [21].

The results of figure 3 also show some adsorption kinetic characters. When NH₃ approaches the 1–4–9 surface from the top of atom 4, it will move to the best site quickly without a barrier. When an NH₃ molecule approaches the bridge 5–9 it will move from the top site of atom 5 to the best site with a barrier of 0.09 eV. Figure 3 also shows that there is a close relation between the adsorption energies and the balance heights. Commonly, the adsorption energies increase with increasing balance height.

3.2. Adsorption of ammonia on the tetracapped trigonal prism (C_{3v}) isomer surface

Now we turn to the tetracapped trigonal prism (C_{3v}). For C_{3v} Si₁₀, the bond structure is more complicated. There are four kinds of atom, each for one layer: 1–3 for Si(A), 4–6 for Si(B), 7 for Si(C), and 8–10 for Si(D). As with T_d Si₁₀, we first try the atop site adsorption, for Si(A)–Si(D). Figure 4 shows the adsorption energies versus adsorption heights for each kind of Si. The adsorption energies are 1.74, 0.70, 0.99, and 0.33 eV for balance heights of 3.91, 4.01, 3.98, and 4.65 au, respectively. Figure 1 shows that Si(A) is hexacoordinated, but it is surprising that when NH₃ approaches the atop site of Si(A), it is most stable. So we calculated the bond order between each kind of Si. We found that the bond order is 0.07 between atoms 1 and 2 (Si(A) and Si(A)) and 0.29 between atoms 1 and 4 (Si(A) and Si(B)), but it is 0.72 between atoms 1 and 7 (Si(A) and Si(C)) and 0.60 between atoms 1 and 8 (Si(A) and Si(D)). This means that atom 1 (Si(A)) binds with atoms 7, 8, and 10, but not with atoms 2–4. On the other hand, the bond angle of atoms 7–1–8 or 7–1–10 is 103.3° and the 8–1–10 bond angle is 115.7°, comparing with 109.5° for standard sp³ hybridization. All these data show that Si(A) binds with three other atoms by sp³ hybridization, and it has one dangling bond. This is why the NH₃ can adsorb atop of Si(A) with maximum adsorption energy.

Figures 5–7 show the adsorption energies and the balance heights for a series of adsorption sites. Just as in figure 3, the reaction coordinates of figures 5(b, d), 6(b), and 7(a, c) mean rotation angles. From figure 5, we can see that the most favoured adsorption site is just atop atom 2 (Si(A)), and the adsorption energy is 1.74 eV.

In particular, we can find in figure 6 that when NH₃ rotates on the top of atom 7 (Si(C)), the total energies have two local minima just as atom 9 does in T_d Si₁₀. Atom 7 is a tricoordinated capped atom and it has a threefold symmetry axis, but the bond angle is 73.3°. These are similar to those of atom 9 of T_d Si₁₀, so we may draw the conclusion that when Si is tricoordinated and has a threefold symmetry axis in the Si cluster, but the bond angle is much smaller than 109.5° for standard sp³ hybridization, only one of its sp³ hybridization orbitals contributes in binding with another atom, i.e. to form a many-centre bond, and this atom may have three dangling bonds.

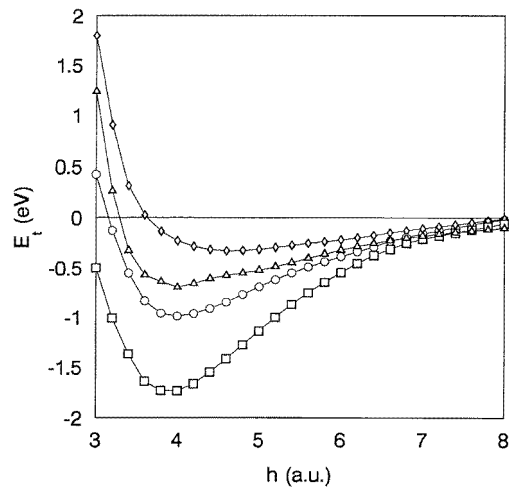


Figure 4. The total energy of the C_{3v} Si_{10} - NH_3 cluster versus the N-Si distance h : \square , Si(A); Δ , Si(B); \circ , Si(C); \diamond , Si(D).

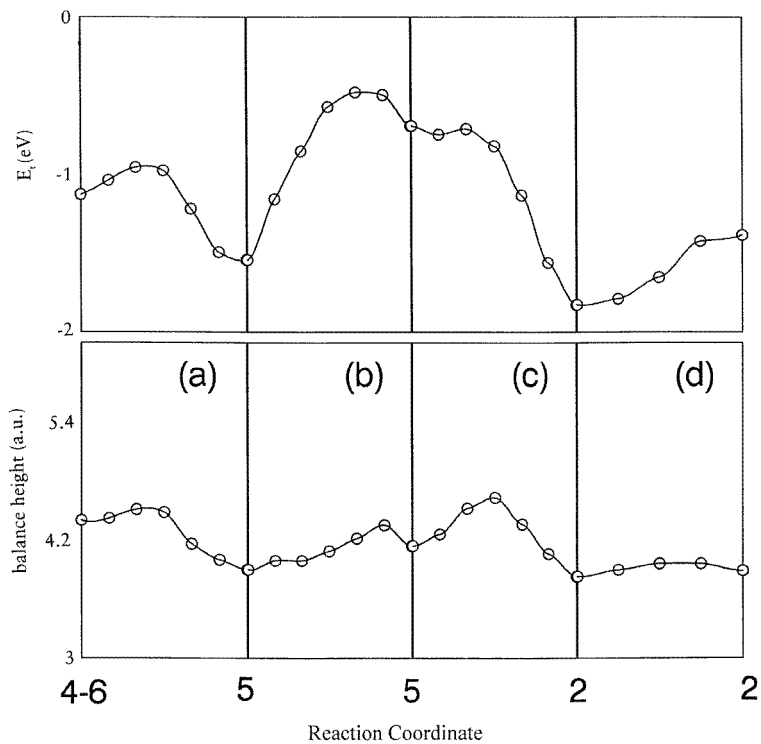


Figure 5. The adsorption energy and balance height of the C_{3v} Si_{10} - NH_3 cluster versus the reaction coordinate for (a) moving from bridge 4-6 to atom 5, (b) rotating atop of atom 5, (c) moving from atom 5 to atom 2, and (d) rotating atop of atom 5.

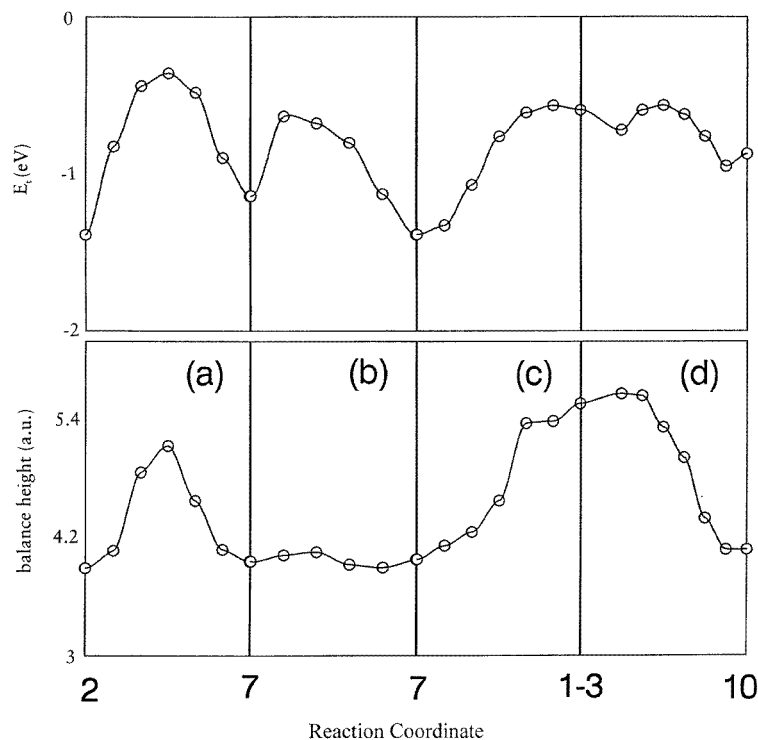


Figure 6. The adsorption energy and balance height of the C_{3v} Si₁₀-NH₃ cluster versus the reaction coordinate for (a) moving from atom 2 to atom 7, (b) rotating atop of atom 7, (c) moving from atom 7 to bridge 1-3, and (d) moving from bridge 1-3 to atom 10.

3.3. Dissociative adsorption: NH₂+H

In order to have a clear picture of the dissociation process, we let one of the three hydrogen atoms (named H(1)) be drawn from the molecule NH₃. For T_d Si₁₀, we first let one NH₃ molecule adsorb on the best site near atom 5, and then draw the H(1) atom from it. Because there are three possible adsorption sites around atom 5, the lowest-energy reaction coordinate is chosen as rotation angles around this atom from the original position of H(1) to another possible adsorption site. For each rotation angle, we change the N-H distance to find a minimum of the total energy. Then the optimized dissociation path is obtained. For C_{3v} Si₁₀, the NH₃ adsorbs atop of atom 2 and then H(1) is drawn to the dangling bond of atom 1. The corresponding variation of the total energies is shown in figure 8 for T_d Si₁₀ and figure 9 for C_{3v} Si₁₀. Here we have assumed the total energy of NH₃ adsorbing on the Si₁₀ cluster surface to be zero. The results show that there is an activation barrier of about 4.63 eV for T_d Si₁₀ and 2.58 eV for C_{3v} Si₁₀ in these processes. It is clear that NH₃ cannot adsorb dissociatively on either the T_d Si₁₀ or the C_{3v} Si₁₀ surface.

We think that the dissociation of NH₃ is decided by two factors. One is whether the NH₃ molecule is made active by the surface or not. When the NH₃ molecule adsorbs on a surface, an electron will transit from NH₃ to the surface because it has a lone pair which can contribute an electron. This charge transition will decrease the dissociative energy of NH₃. The other factor is whether there is another dangling bond near the NH₃ or not, which can accept the hydrogen atom. So we first calculate the intrinsic dissociative energy for a

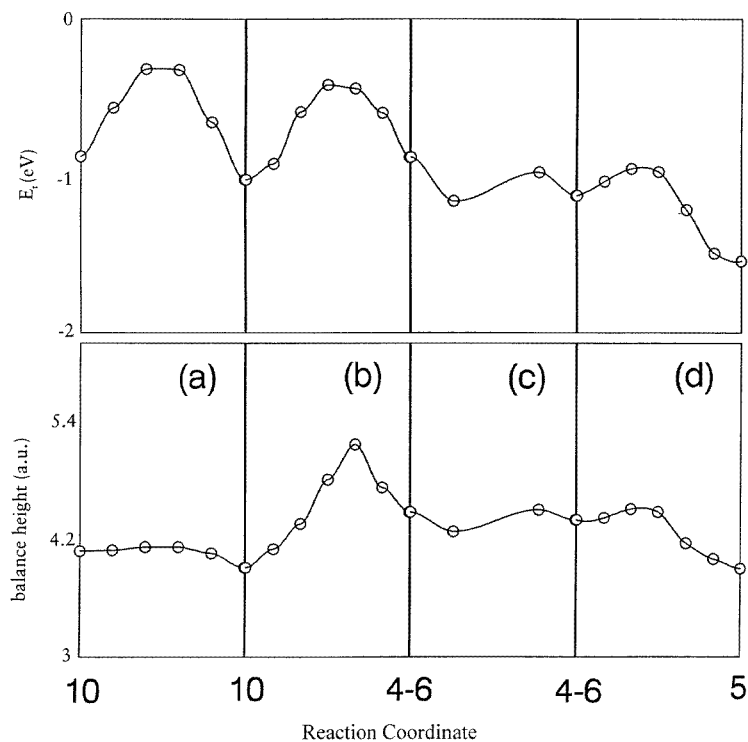


Figure 7. The adsorption energy and balance height of the C_{3v} Si_{10} - NH_3 cluster versus the reaction coordinate for (a) rotating atop of atom 10, (b) moving from atom 10 to bridge 4-6, (c) rotating atop of bridge 4-6, and (d) moving from bridge 4-6 to atom 5.

hydrogen atom being drawn from the NH_3 molecule to an infinite distance (see table 1). The result is 6.68 eV (E_{i0}) for the free NH_3 molecule. When NH_3 adsorbs on the T_d Si_{10} surface, the intrinsic dissociative energy is 6.21 eV (E_{i1}) for T_d Si_{10} and 5.02 eV (E_{i2}) for C_{3v} Si_{10} . However, when NH_3 adsorbs on the $Si(100)$ - 2×1 surface, this intrinsic dissociative energy is only 4.10 eV (E_{i3}). The decrease in intrinsic dissociative energy demonstrates that the ammonia molecule is made active by the adsorbent, and the contribution from adsorbent can be calculated from $E_{in} - E_{i0}$ ($n = 1, 2, 3$). The results show that the $Si(100)$ - 2×1 surface can make the ammonia mostly active. As mentioned above, sp^3 hybridization of C_{3v} Si_{10} is better than that of T_d Si_{10} , but is worse than that of $Si(100)$ - 2×1 , so the intrinsic dissociation energy decreases in the order of $Si(100)$ - 2×1 , C_{3v} Si_{10} , T_d Si_{10} . On the other hand, because there is another dangling bond near the NH_3 on the $Si(100)$ - 2×1 surface, but for C_{3v} Si_{10} and T_d Si_{10} another dangling bond is too far from the NH_3 , the contributions of calculated activation energies from another dangling bond are -4.10 eV for the $Si(100)$ - 2×1 surface, -2.44 eV for C_{3v} Si_{10} , and -1.58 eV for T_d Si_{10} , as shown in table 1. (This is calculated from $E_{in} - E_{Bn}$ ($n = 1, 2, 3$)). All these results confirm the view that NH_3 cannot dissociate on the Si_{10} cluster surface. In particular, the difference in H dissociation barriers between the two Si_{10} isomers also arises from these two facts: sp^3 hybridization of C_{3v} Si_{10} is better than that of T_d Si_{10} , and the nearby dangling bond of C_{3v} Si_{10} is better and closer than that of T_d Si_{10} .

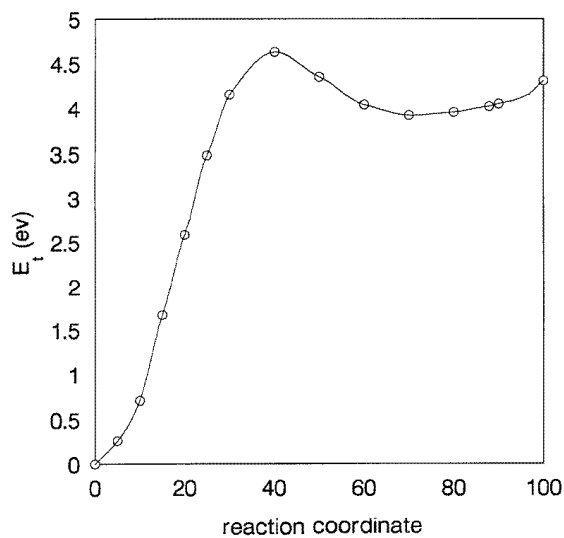


Figure 8. The variation of the total energy of H dissociation versus reaction coordinate for NH₃ for T_d Si₁₀. The reaction coordinate is chosen as the rotation angles around atom 5 from the original position to another possible adsorption site.

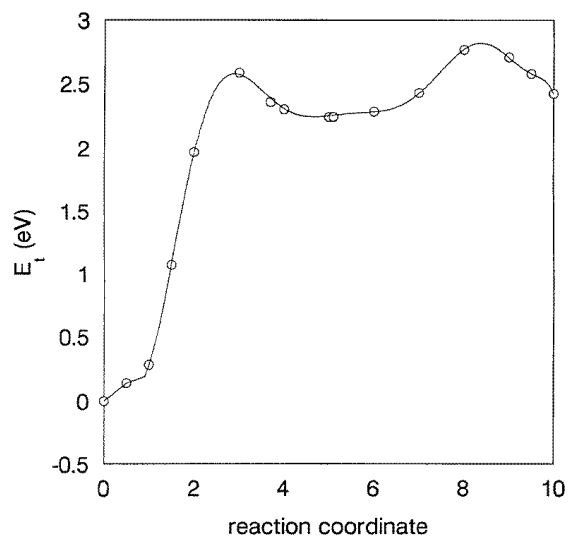


Figure 9. The variations of the total energy of H dissociation versus reaction coordinate for NH₃ for C_{3v} Si₁₀. The reaction coordinate is the distance between the original position of the H atom and atom 1 of C_{3v} Si₁₀.

4. Summary

From the theoretical analysis presented above we have observed the nature of the NH₃ molecule adsorption processes on Si₁₀ clusters by the DV-X_α method. We have considered two isomers of Si₁₀. For T_d Si₁₀, the best adsorption site is near the Si(B) atom, which has three dangling bonds from sp³ hybridization orbitals, and the remaining orbital binds with

Table 1. Intrinsic dissociative energy (eV) of NH_2+H for varying adsorbent, and the contribution from two factors: adsorbent activation and a nearby dangling bond, which decrease the H dissociation energy of NH_3 .

	NH_3 $n = 0$	$\text{T}_d \text{ Si}_{10}$ $n = 1$	$\text{C}_{3v} \text{ Si}_{10}$ $n = 2$	$\text{Si}(100)\text{-}2 \times 1$ $n = 3$
Intrinsic dissociative energy (E_{in})	6.68	6.21	5.02	4.10
Activation energy by adsorbent	—	-0.47	-1.66	-2.58
Contribution from nearby dangling bond	—	-1.58	-2.44	-4.10
H dissociation barrier (E_{Bn})	6.68	4.63	2.58	0.00 [19]

three Si(A) atoms to form many-centre bonds. The adsorption energy is 1.15 eV. For $\text{C}_{3v} \text{ Si}_{10}$, the best adsorption site is atop the Si(A) atom, which has one dangling bond from sp^3 hybridization orbitals, and the other orbitals bind with one Si(C) and two Si(D) atoms. The adsorption energy is 1.74 eV.

When we draw an H atom from an adsorbed NH_3 molecule, there exist activation barriers for both $\text{T}_d \text{ Si}_{10}$ and $\text{C}_{3v} \text{ Si}_{10}$. The barrier is decided by two factors. One is whether the NH_3 molecule is made active by the surface or not. The other is whether there is another dangling bond near the NH_3 or not. Because the $\text{Si}(100)\text{-}2 \times 1$ surface activates the NH_3 most, and there is a neighbour dangling bond, the barrier is zero for the NH_2 molecule on such a surface. However, the activation of the adsorbed NH_3 molecule is not good enough for Si_{10} clusters, and another dangling bond is too far from this molecule, so the activation barriers are 4.63 eV for $\text{T}_d \text{ Si}_{10}$ and 2.58 eV for $\text{C}_{3v} \text{ Si}_{10}$, and NH_3 cannot dissociate on either $\text{T}_d \text{ Si}_{10}$ or $\text{C}_{3v} \text{ Si}_{10}$ surfaces.

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