

Supplementary information

Chemisorption of Silicon Tetrachloride on Silicon Nitride: A Density Functional Theory Study

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Bond dissociation energy

Figure S1 shows the bond dissociation energy (BDE) associated with the SiCl_4 surface reactions described in the main manuscript. The bond dissociation energy was determined using the following equation:

$$\text{BDE} = H^\circ(\text{A}) + H^\circ(\text{B}) - H^\circ(\text{A} - \text{B}) \quad (1)$$

where H° is the standard absolute enthalpy obtained from the DFT calculation. The details of the BDE calculation method have been discussed in the literature.^{1,2} The sample molecules were chosen to represent the environment of the dissociated bond.


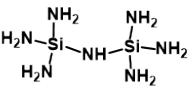
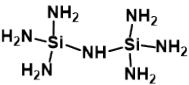

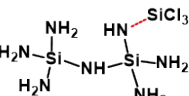
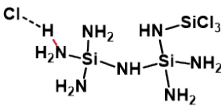
Bond	Model schematic	BDE (eV)
Si-Cl		4.57
N-H from NH_2		4.57
N-H from NH		4.53
H-Cl		4.53
Si-N		4.82
N-H		3.40

Fig. S1 BDE values of bonds associated with the SiCl_4 surface reaction and the model structure used to calculate them.

Atomistic structures of reactant states with adjacent NH₂ sites

Figure S2 shows the planar views of the surface sites used in the reactant states **R1**, **R2**, and **R3**, respectively. The NH₂ sites to which the H1, H2, and H3 atoms will migrate to form the NH₃⁺Cl⁻ complexes are marked with red circles.

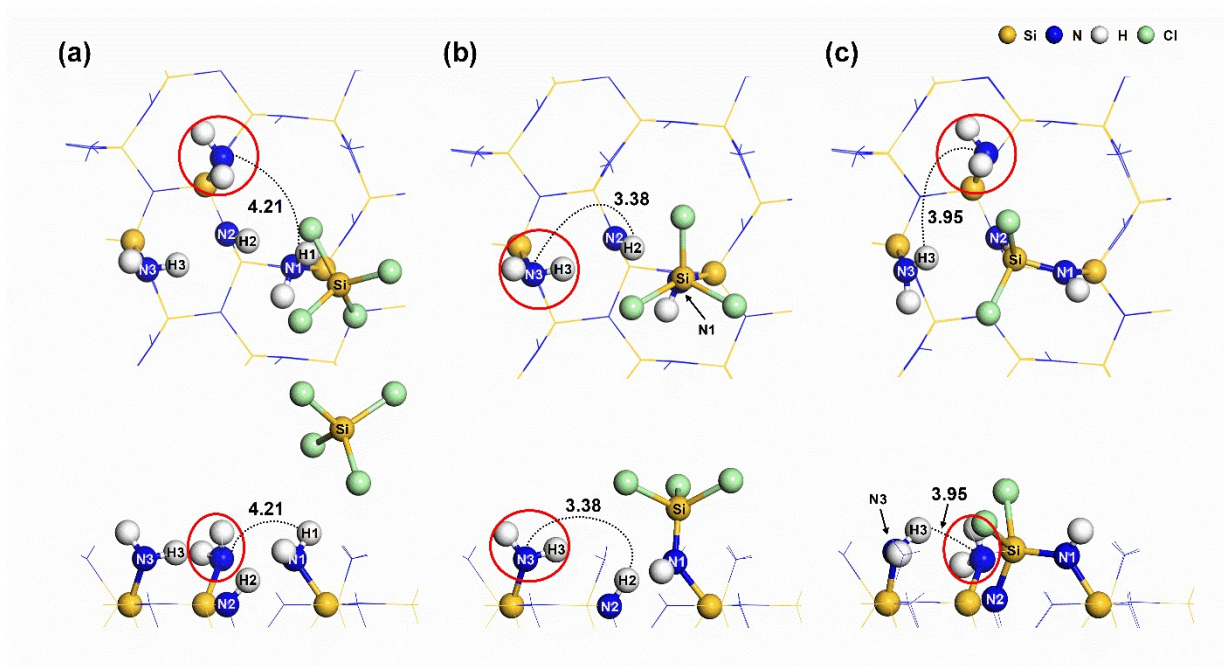


Fig. S2 The atomistic structures of the reaction sites along with the adjacent NH₂ sites for H atom migration in (a) **R1**, (b) **R2**, and (c) **R3**. A planar view is shown at the top, and the cross-sectional view at the bottom. The dotted lines represent the interatomic distances with corresponding values in Å.

Atomistic structure showing subsurface bonds

Figure S3 shows the subsurface bonds of the **R2** and **P2** states. The two Si–N₂ subsurface bonds were stretched from 1.72 Å and 1.74 Å in **R2** to 1.79 Å and 1.84 Å in **P2**, respectively.

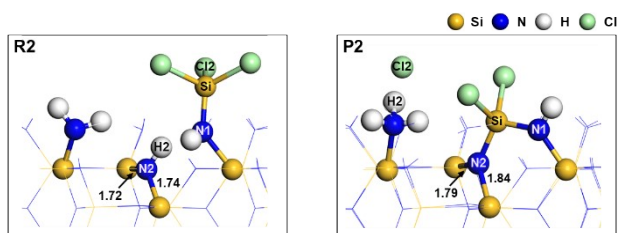


Fig. S3 The atomistic structure of the reactant (**R2**) and product (**P2**) states showing the Si–N2 subsurface bonds. The bond lengths are shown in Å.

Mulliken atomic charges for **R2**, **TS2**, **P2**, **R3**, **TS3**, **P3** states

Table S1 and S2 show the change in Mulliken atomic charges for the second and third reactions. The trend remains consistent with the change from **R1** to **P1b**.

Table S1: The Mulliken atomic charges for **R2**, **TS2**, and **P2** states.

Atom	Mulliken charge (e)		
	R2	TS2	P2
Si	1.310	1.375	1.419
Cl2	-0.405	-0.381	-0.691
N2	-1.147	-1.275	-1.328
H2	0.325	0.224	0.303

Table S2: The Mulliken atomic charges for **R3**, **TS3**, and **P3** states.

Atom	Mulliken charge (e)		
	R3	TS3	P3
Si	1.410	1.467	1.461
Cl3	-0.448	-0.507	-0.712
N3	-0.792	-1.075	-1.005
H3	0.216	0.328	0.312

References

- 1 A. K. Chandra and T. Uchimaru, *J. Phys. Chem. A*, 2000, **104**, 9244–9249.
- 2 S. J. Blanksby and G. B. Ellison, *Acc. Chem. Res.*, 2003, **36**, 255–263.