Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Atomic layer deposition of diisopropylamino silane on WO_3(001) and W(110): a density functional theory study

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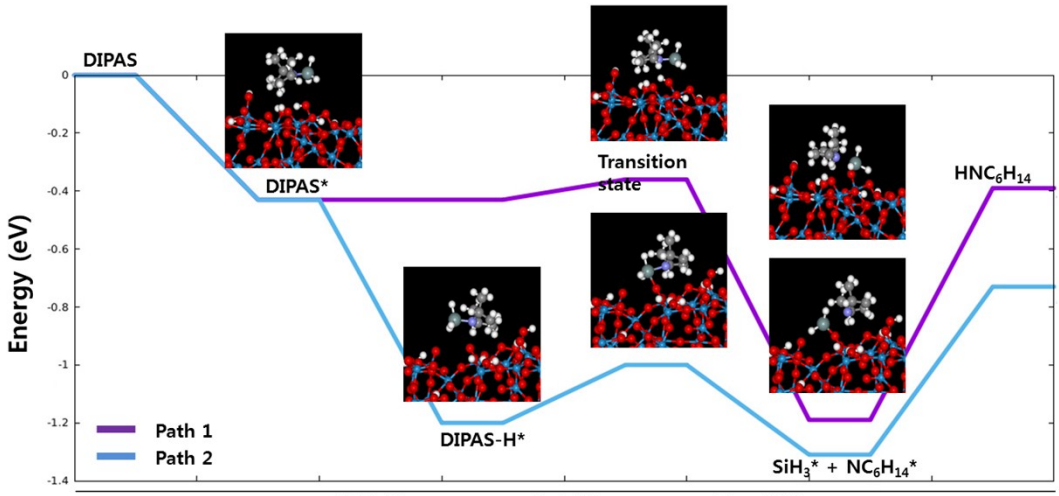


	ΔE (eV)	E_a (eV)	E_{ads} (eV)
Path 1	-0.86	0.07	-0.43
Path 2	-0.11	0.20	-1.20

Figure S1. Si-N dissociation of DIPAS on the hydroxylated amorphous WO_3 surface. While there is no H transfer during DIPAS adsorption in Path 1, the H transfer from the surface OH group to the N atom of DIPAS takes place in Path 2. Red spheres, O; blue spheres, W; Iris blue spheres, N; large gray spheres, Si; small gray spheres, C; white spheres, H.

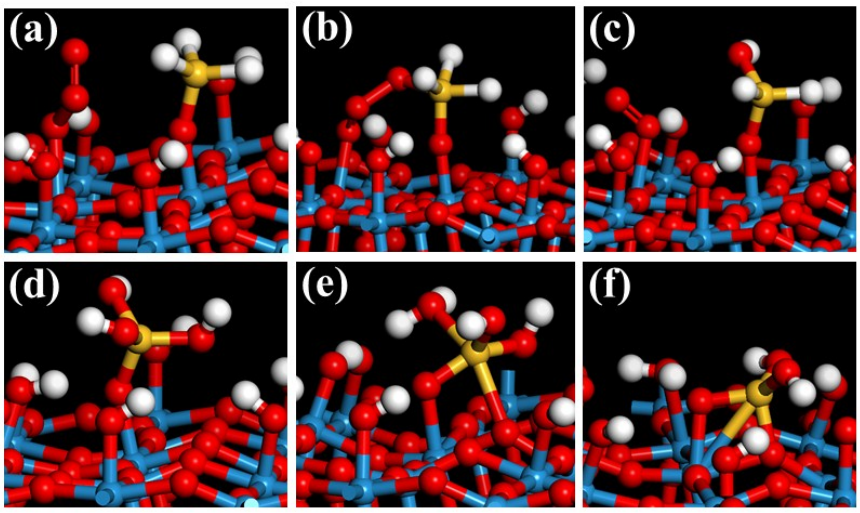


Figure S2. Dissociation of SiH_3 on the hydroxylated WO_3 surface through a two- step process: Oxidation of SiH_3 to $Si(OH)_3$ by ozone (a, initial; b, transition; c, final state) and then dehydration of $Si(OH)_3$ to SiH_3 (d, initial; e, transition; f, final state)

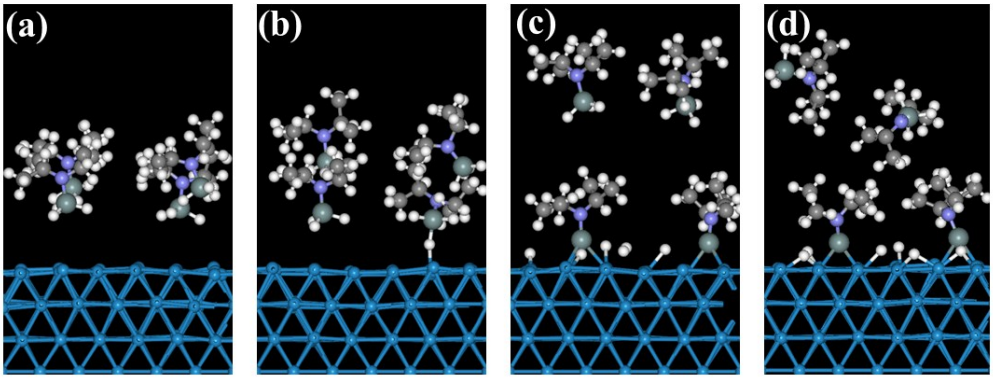


Figure S3. Snapshots during the decomposition of DIPAS molecules on W(110) at (a) 120, (b) 380, (c) 1320, and (d) 3720 fs in an AIMD trajectory

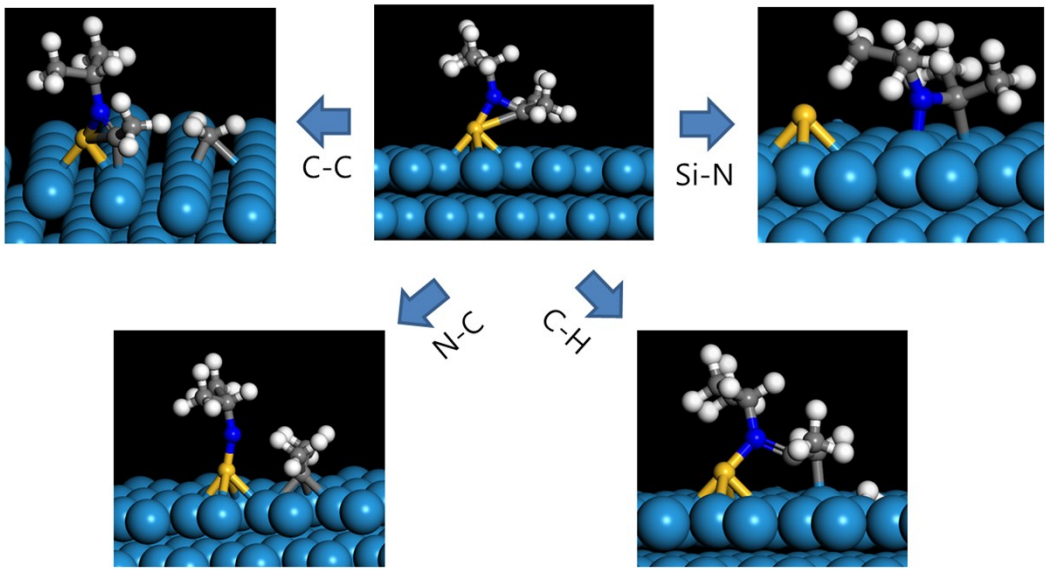
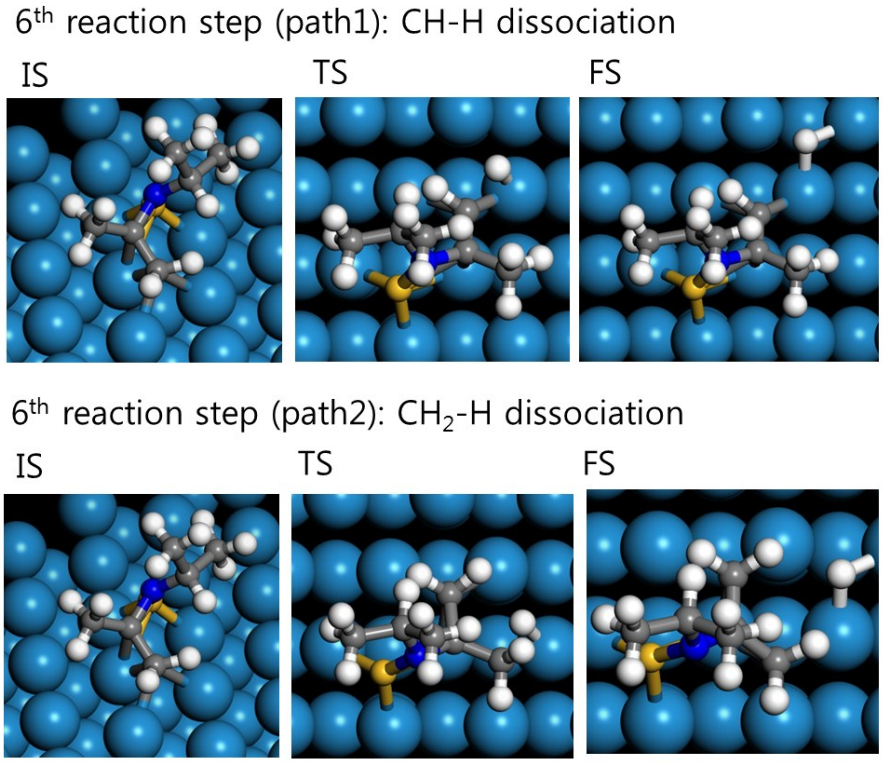
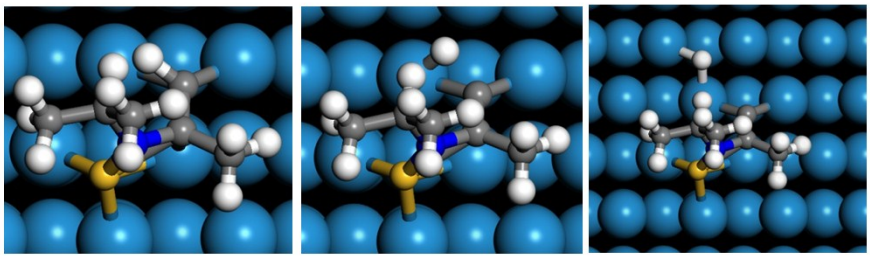


Figure S4. Four reaction paths for $SiNC_6H_{13}$* decomposition: Si-N, C-H, N-C, and C-C dissociation



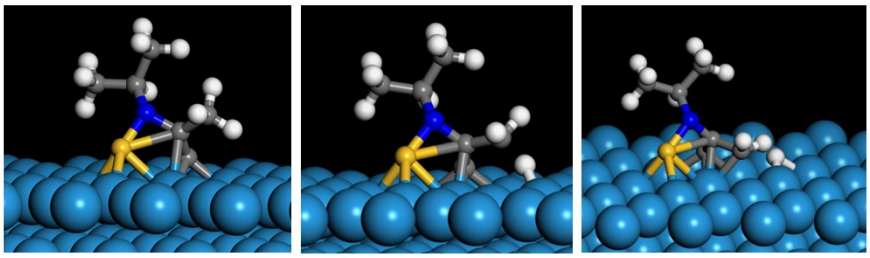
7th reaction step: C-H dissociation

IS TS FS



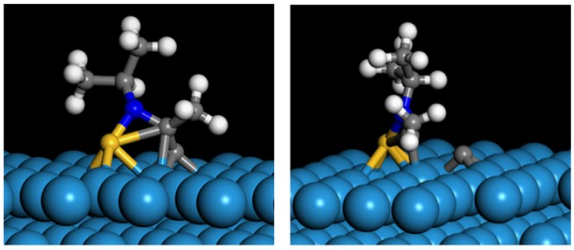
8th reaction step (path1): C-H dissociation

IS TS FS



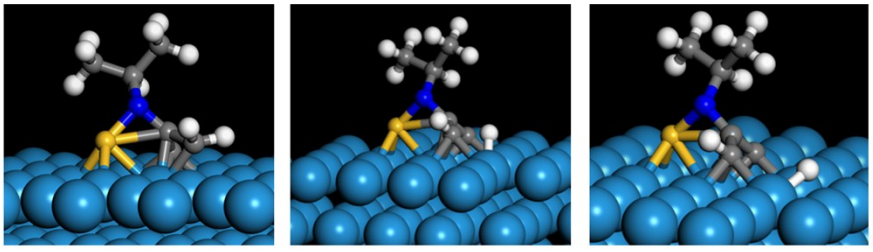
8th reaction step (path2): C-C dissociation

IS FS



9th reaction step (path1): C-H dissociation

IS TS FS



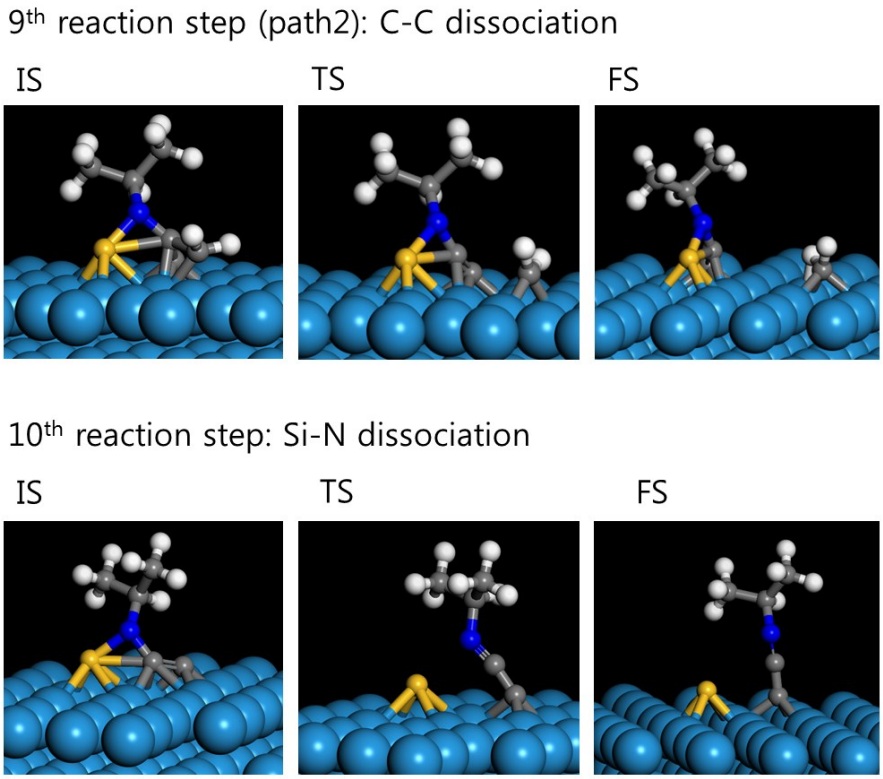


Figure S5. Initial (IS), transition (TS), and final (FS) states of intermediate reactions from the 6th reaction step to the 10th reaction step. In the case of the 8th reaction step (path2), the transition state image is not included because the transition state is similar to the final state.

Table S1. Activation energies (E_a, eV) and reaction energies (E_{rxn}, eV) of SiH_3 dissociation on the hydroxylated WO_3 (001) surface in the presence of ozone.

Reaction	Step1: oxidation	Step2: dehydration
	$SiH_3 + O_3 \rightarrow SiH_2(OH) + O_2$	$SiH_2(OH) + OH \rightarrow SiH_2 + H_2O$
E_a	0.74	1.10
E_{rxn}	-3.38	-0.73

Table S2. Activation energies (E_a, eV) and reaction energies (E_{rxn}, eV) of DIPAS

decomposition on the W (110) surface

reaction step	dissociation	E_a (eV)	E_{rxn} (eV)
step 1	Si-H	0.00	-0.63
step 2	Si-H	0.00	-1.25
step 3	Si-H	0.08	-1.08
	Si-N	1.72	-2.19
step 4	Si-N	1.81	-1.29
	N-C	2.33	-0.55
	C-C	1.48	-0.45
	C-H	0.61	0.01
step 5	Si-N	0.97	-2.11
	C-H	0.40	-0.67
	N-C	1.07	-0.85
	C-C	1.01	-0.90
step 6	CH-H	0.43	-0.32
	CH_2-H	1.00	-1.03
step 7	C-H	0.17	-0.55
step 8	C-H	1.02	-0.52
	C-C	0.71	0.71
step 9	C-H	0.39	-0.29
	C-C	0.32	-1.32
step 10	Si-N	1.06	-0.43