Electronic Supplementary Information

Mechanistic Insight into the Hydrazine Decomposition on Rh(111): Effect of Reaction Intermediate on Catalytic Activity

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Fig. S1. The metastable adsorption configurations involved in hydrazine decomposition on Rh(111).

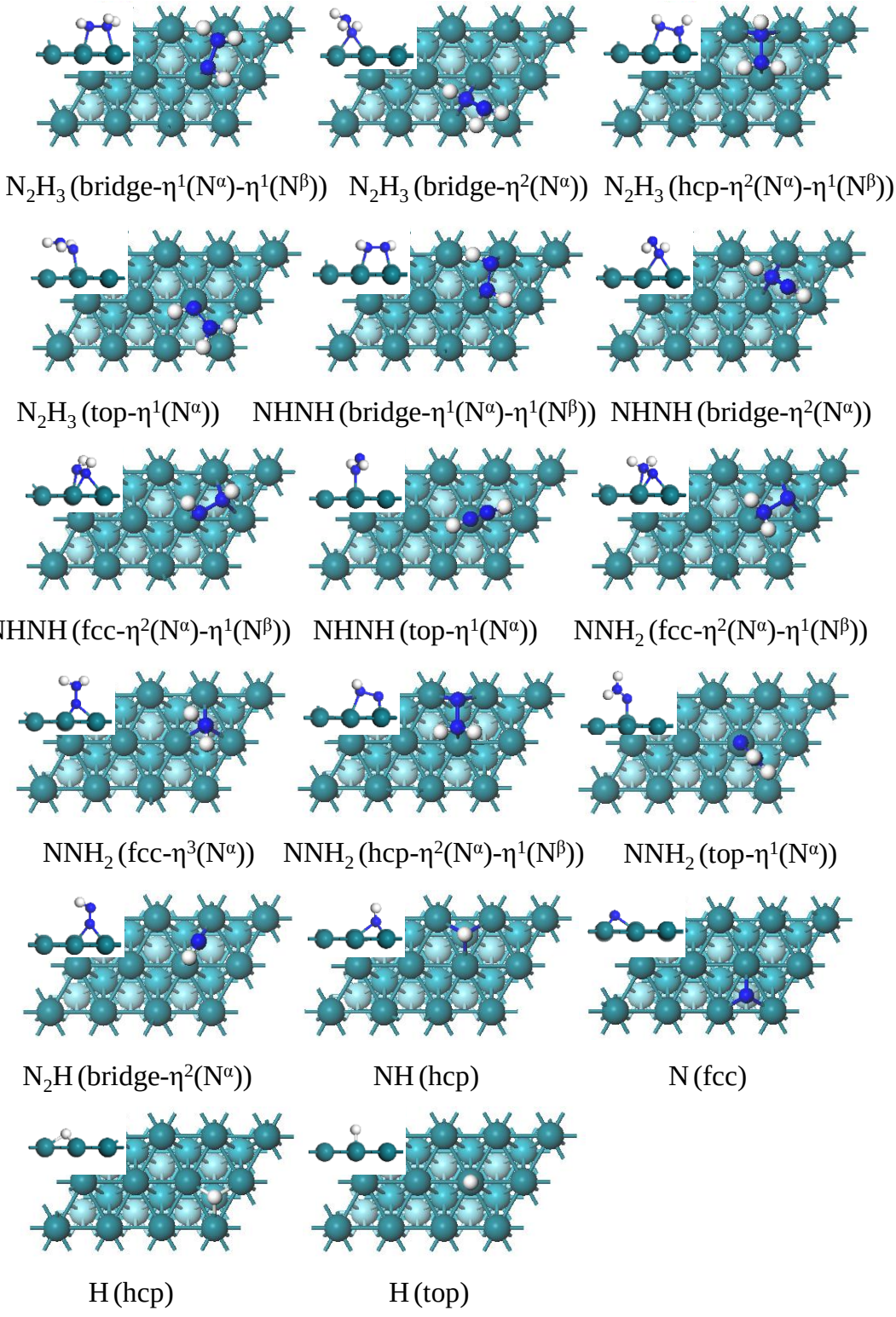


Fig S2. Elementary steps of intramolecular N_2H_4 decomposition on Rh(111) (2×2) slab.

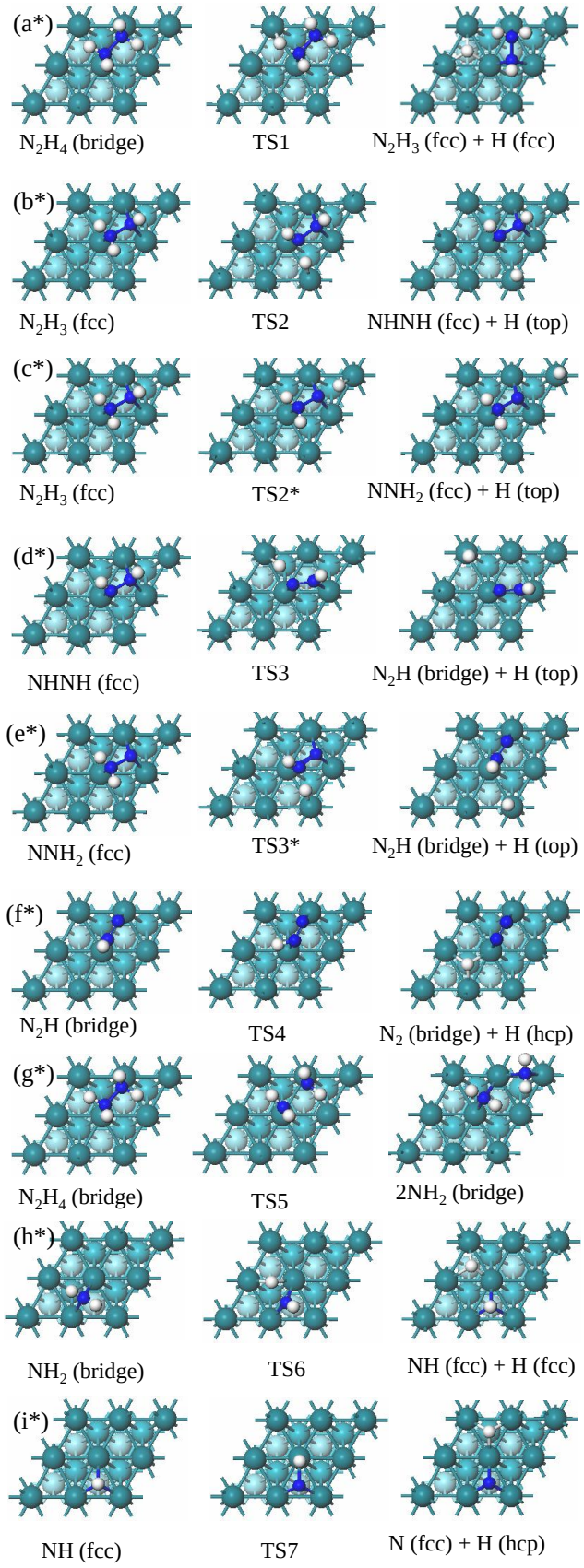
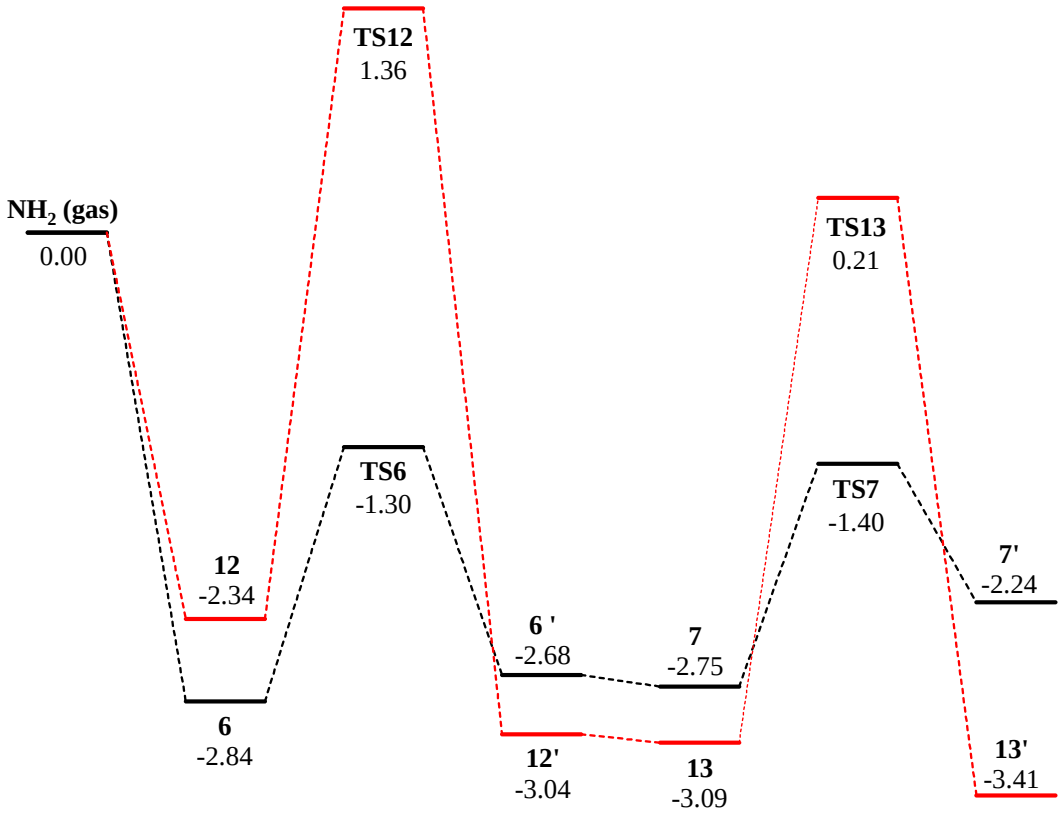


Fig. S3 PESs of NH_2 decomposition on Rh(111). The energy reference corresponds to the total energy of one gas-phase NH_2, one clean slab, and two adsorbed NH_2 fragment.



6, $NH_2^* + 2NH_2^*$; **6'**, $[NH + H]^* + 2NH_2^*$; **7**, $NH^* + H^* + 2NH_2^*$; **7'**, $[N + H]^* + H^* + 2NH_2^*$; **12**, $[NH_2 + NH_2]^* + NH_2^*$; **12'**, $[NH + NH_3]^* + NH_2^*$; **13**, $[NH + NH_2]^* + NH_3^*$; **13'**, $[N + NH_3]^* + NH_3^*$.

Table S1 Coadsorption configurations, coadsorption energies (in eV), and structural parameters (in angstroms) for the coadsorption systems involved in NH_2-assisted hydrazine decomposition on Rh(111).

System	E_{ads}	$d_{N–N}$[a]	$d_{N–Rh}$[b]	$d_{N–H}$[a]
N_2H_4 (bridge) + NH_2 (bridge)	3.67	1.450	2.248, 2.248	1.027, 1.027, 1.030, 1.031
N_2H_3 (fcc) + NH_2 (bridge)	4.80	1.439	2.118, 2.152, 2.165	1.025, 1.027, 1.027
NHNH (hcp) + NH_2 (bridge)	4.41	1.393	2.082, 2.094, 2.123	1.027, 1.032
NNH_2 (fcc) + NH_2 (bridge)	6.01	1.436	2.056, 2.068, 2.126	1.026, 1.027
N_2H (bridge) + NH_2 (bridge)	4.58	1.254	1.963, 2.079	1.035

[a] The N–N and N–H bonds in the N_2H_x fragment. [b] The distance between the N atoms of N_2H_x and surface Rh atoms.

Table S2 Energy barriers E_a and reaction energies ΔE (in eV) for the elementary steps involved in intramolecular hydrazine decomposition on Rh(111) (2×2) slab.

Reactions	E_a	ΔE
(a*) $N_2H_4 \rightarrow N_2H_3 + H$	0.75	-0.30
(b*) $N_2H_3 \rightarrow NHNH + H$	1.07	0.63
(c*) $N_2H_3 \rightarrow NNH_2 + H$	1.50	0.46
(d*) $NHNH \rightarrow N_2H + H$	1.04	0.11
(e*) $NNH_2 \rightarrow N_2H + H$	1.12	0.20
(f*) $N_2H \rightarrow N_2 + H$	0.99	-0.28
(g*) $N_2H_4 \rightarrow 2NH_2$	0.46	-0.81
(h*) $NH_2 \rightarrow NH + H$	1.53	0.24
(i*) $NH \rightarrow N + H$	1.29	0.57

Table S3 Diffusion barrier (E_{diff}), reaction energy (ΔE) (in eV) for the diffusion of some species on Rh(111)- (2×3) slab.

Diffusion	E_{diff}	ΔE
N_2H_4 (top) → N_2H_4 (bridge)	0.03	0.01
N_2H_4 (bridge) + NH_2 (bridge-1) → N_2H_4 (bridge) + NH_2 (bridge-2)	0.39	0.04
N_2H_4 (top) + NH_2 (bridge-1) → N_2H_4 (bridge) + NH_2 (bridge-2)	0.69	0.21