Volcano Curves for in Silico Prediction of Mono- and Bifunctional Catalysts: Application to Ammonia Decomposition

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Table S1. BEP relations between activation energy (E_a) and reaction energy (E_{rxn}) for NH_x^* dissociation and N^*- N^* association reactions approximated with $E_a = mE_{rxn} + n$. Energies are in kcal/mol. H_2 and N_2 adsorptions are treated as barrierless.

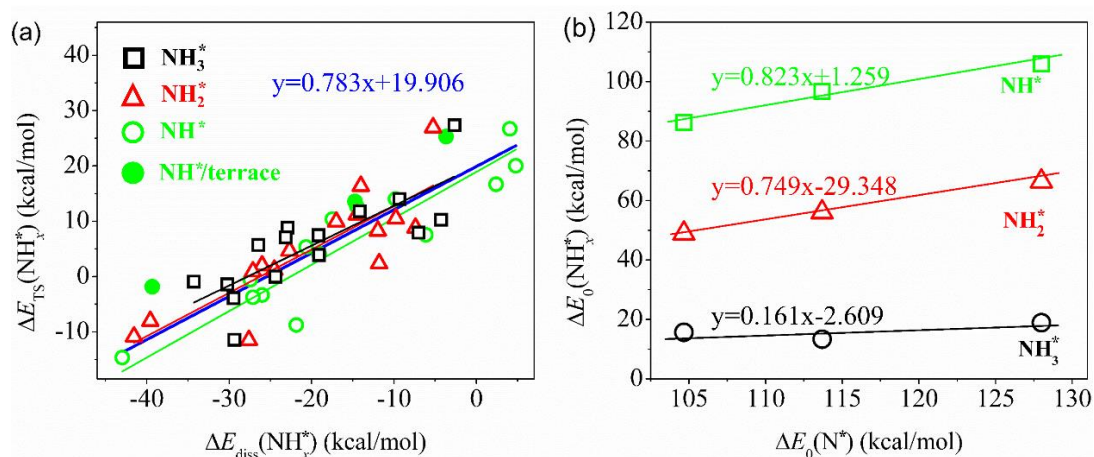| Reaction	m	n
NH_3^* dissociation	0.71	23.23
NH_2^* dissociation	0.52	19.83
NH^* dissociation	0.29	23.75
N_2^* association on terrace	0.33	50.04
N_2^* association at edge	0.32	40.36

Figure S1. Thermochemical scaling relations (TCSRs) for NH_3 decomposition reaction on various transition metal/bimetallic facets. (a) Universal transition state scaling relation (TSSR) between $\Delta E_{TS}(NH_x^*)$ and $\Delta E_{diss}(NH_x^*)$ of NH_x^* dehydrogenation reactions. The solid symbols in green color are based on our DFT calculations, and the rest of the data is from literature. The blue solid line is the universal TSSR model. NH_3 in the gas-phase is used as the reference state. (b) TCSR between $\Delta E_0(NH_x^*)$ and $\Delta E_0(N^*)$ on Ni, Pt and Ni-Pt-Pt terrace sites. The TCSRs of NH and NH_2 agree well with previous literature[1], and the NH_3 scaling is based on our own published DFT data[2].
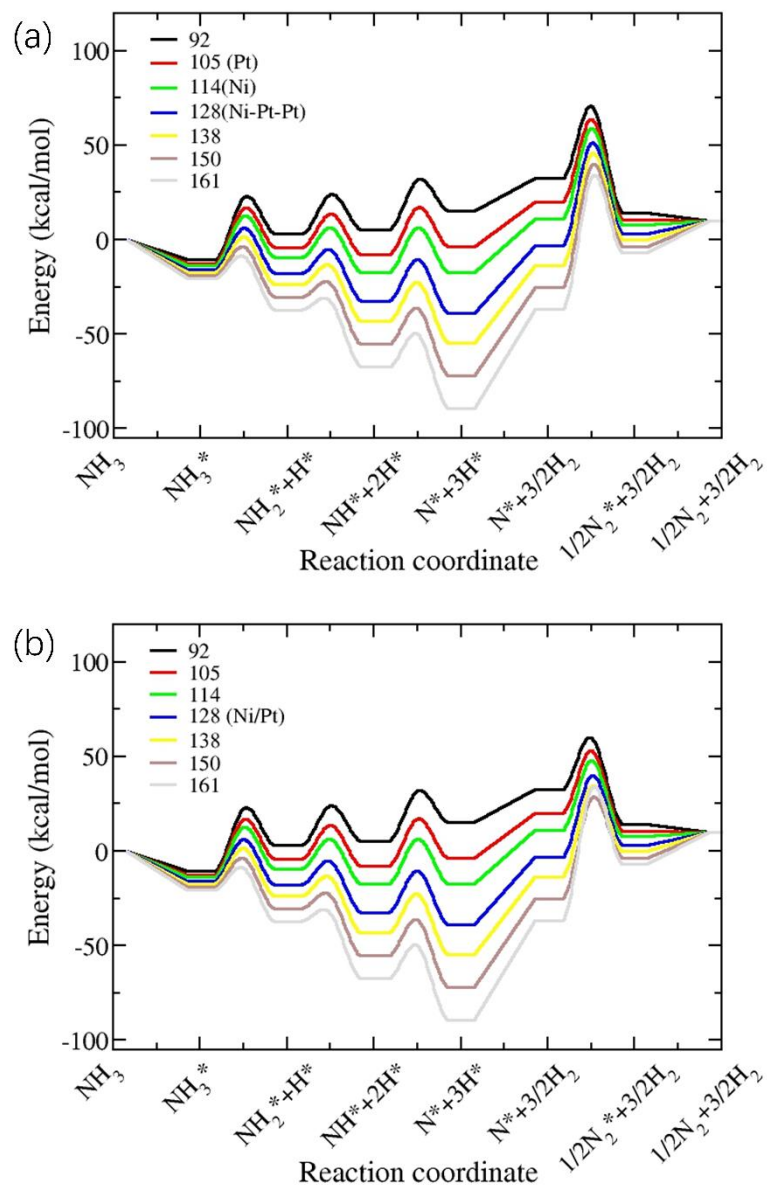
Figure S2. Energy profiles calculated with TCSR and TSSR as input (a) for perfect and (b) defected surfaces. The numbers in the legend indicate the value of $\Delta E_0(N^*)$ on each surface.

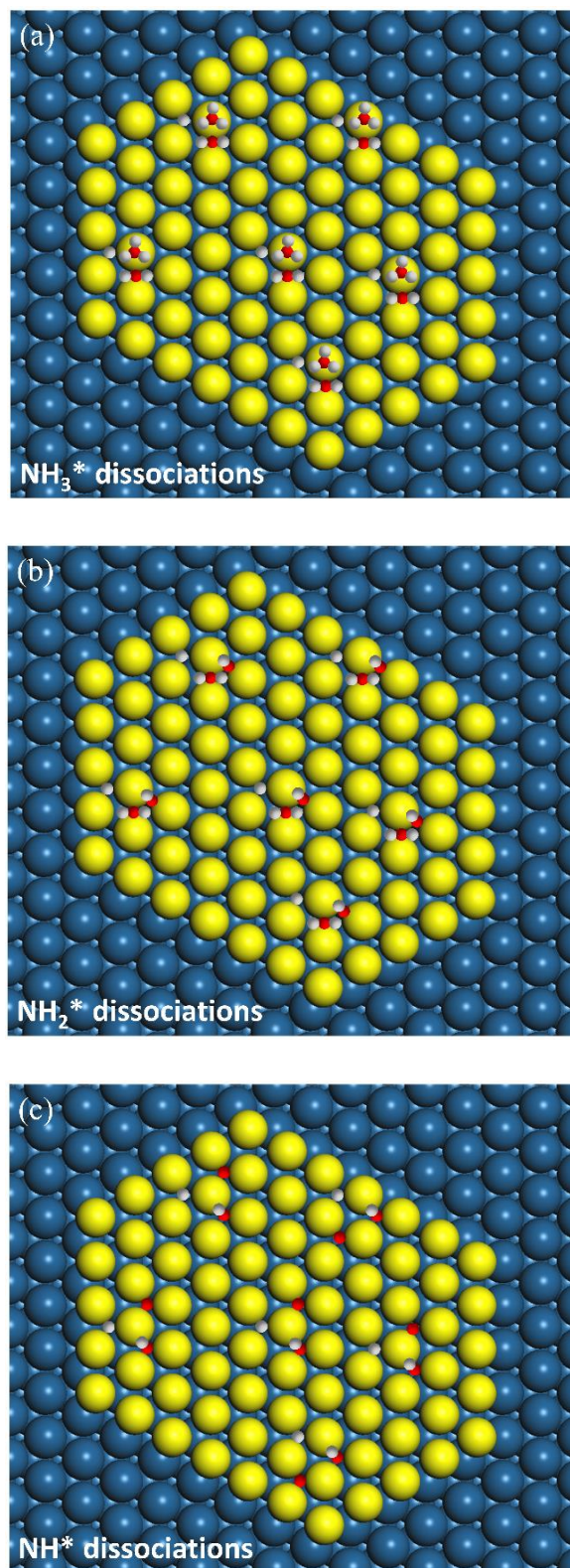**Figure S3.** Schematics of the NH_3 stepwise decomposition and corresponding reaction intermediates and active sites distribution on sub-monolayer surfaces of 79 guest atoms on FCC(111) host, considered in the KMC simulations. Panels from top to bottom are for the elementary steps of NH_3^* dissociation, NH_2^* dissociation, and NH^* dissociation, respectively. The yellow, dark blue, red and white spheres denote guest, host, N and H atoms, respectively.
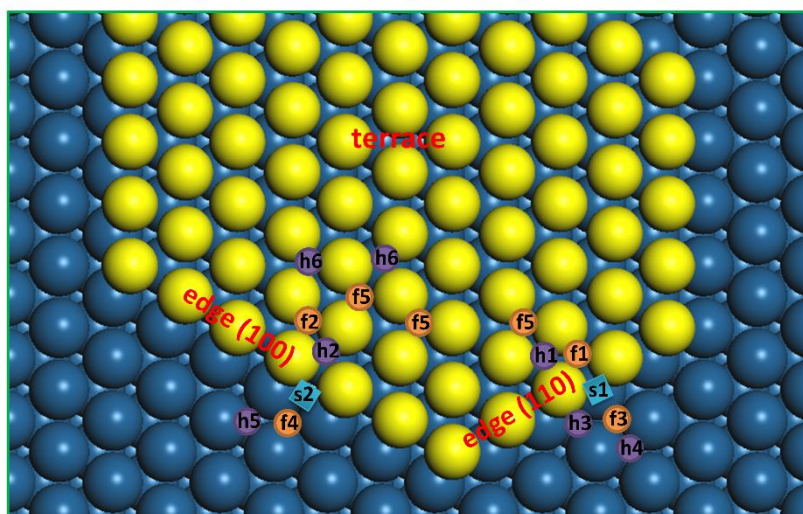
Figure S4. Schematic illustration of the reaction sites considered in the KMC simulations. The labels "f", "h", and "s" represent fcc hollow sites, hcp hollow sites, and step sites, respectively.

Table S2. N* diffusion steps, reaction sites and corresponding original/rescaled N* diffusion barriers in KMC simulations. The sites refer to the labels shown in Fig. S4.

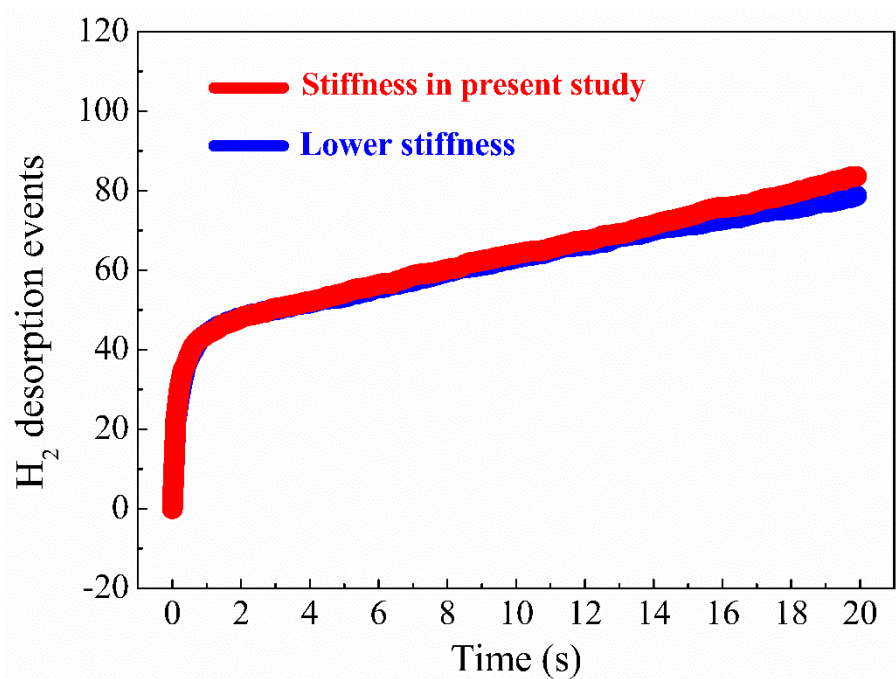| No.	Reaction	Sites	Barriers (Original/Rescaled)
1	N* diffusion	f1, s1	0.81/1.4 eV
2	N* diffusion	f5, h6	0.75/1.2 eV
3	N* diffusion	f5, h1	0.75/1.15 eV
4	N* diffusion	h2, s2	1.21/1.6 eV
5	N* diffusion	f1, f2	0.47/1.1 eV
6	N* diffusion	h1, f2	0.47/0.95 eV
7	N* diffusion	f4, s2	0.36/0.7 eV

Figure S5. Comparison of KMC simulated H_2 desorption rate on bimetallic Ni/Pt surface between stiffness in the resent work and lower stiffness. The rates are averaged from 20 KMC simulations at 673 K and 1.3×10^{-3} bar.

References

(1) Abild-Pedersen, F.; Greeley, J.; Studt, F.; Rossmeisl, J.; Munter, T.; Moses, P. G.; Skulason, E.; Bligaard, T.; Nørskov, J. K. Scaling Properties of Adsorption Energies for Hydrogen-Containing Molecules on Transition-Metal Surfaces. *Phys. Rev. Lett.* **2007**, *99*, 016105.

(2) Guo, W.; Vlachos, D. G. Patched Bimetallic Surfaces are Active Catalysts for Ammonia Decomposition. *Nat. Commun.* **2015**, *6*, 8619.