

Supplementary Information

Thermodynamic and Kinetic Study on Catalytic Performance of Fe, Mo,
Rh and Ru for Electrochemical Nitrogen Reduction Reaction

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Computation of thermodynamics

The Gibbs free energies consist of DFT total energies corrected by zero-point energy (ZPE), heat capacity (C_p), and entropy (TS). In this method, the G is defined as follows:^{1, 2}

$$G = E_{DFT} + E_{ZPE} + \int C_p dT - TS \quad (1)$$

Where E_{DFT} is the energy of most stable configuration, E_{ZPE} is the zero-point energy change, $\int C_p dT - TS$ is the correction for entropy and enthalpy. TS is calculated at temperature of 298.15 K and pressure of 1 atm. The calculated vibrational energies and correction used the VASPKIT code, only $3N$ degrees of freedom of the adsorbates were considered.³ More details of the correction of Gibbs free energy calculated by VASPKIT code are list in Table S3 and Table S4, respectively, for adsorbates and free molecules.

The electroreduction of N_2 contains multiple electron transfers and proton transfers. In this work, a concerted proton-electron transfer process is considered, in which the electron transfer and proton transfer occur simultaneously. For a typical one-electron-one-proton transfer reaction:



The Gibbs free energy change is obtained from the corresponding hydrogenation reaction using the computational hydrogen electrode (CHE) model,⁴ in which the electrochemical potential of a proton-electron pair at $pH = 0$ and $U = 0$ V vs. SHE is scaled to half of the chemical potential of hydrogen gas.

$$\Delta G_{CPET} = G_{*AH} - G_{*A} - 1/2 G_{H_2} \quad (3)$$

The effect of an applied bias, U , was included for all electrochemical reaction steps by shifting the free energy by $-neU$, where n is the number of electrons involved in the reaction.⁵

$$\Delta G(U) = \Delta G^0(U = 0) - neU = -nFE^0 - neU \quad (4)$$

Computation of kinetics

According to the transfer of a proton and electron for a displaced-distorted oscillator model, the computational equation for total reorganization energy is as follows:

$$\lambda_{R/P} = \lambda_{R/P}^i + \lambda_{R/P}^{o,ET} + \lambda_{R/P}^{o,PT} \quad (5)$$

The total reorganization energy is composed of three parts, including λ^i which denotes the internal reorganization energy and λ^o which denotes the solvent reorganization energy. λ^o consists of electron-transfer reorganization energy and proton-transfer reorganization energy. The expression of internal and solvent reorganization energy are given below:

$$\lambda_R^i = E_R(P_e) - E_R(R_e) \quad (6)$$

$$\lambda_P^i = E_P(R_e) - E_P(P_e) \quad (7)$$

Where $E_R(P_e)$ denotes single point energy of the stable configuration of product complexes, $E_P(R_e)$ denotes single point energy of the stable configuration of the reactant complexes. $E_R(R_e)$ and $E_P(P_e)$ are electronic energy of the most stable adsorption configurations of the reactant and product, respectively. To keep the conservation of matter, $E_R(P_e)$ is calculated in the configuration which remove one hydrogen from the product, and $E_P(R_e)$ is calculated in the configuration which add one hydrogen from the reactant.

Solvent reorganization energy related to electron transfer and proton transfer can be calculated as follows:⁶

$$\lambda_{R/P}^{o,ET} = \frac{e_0^2}{4\pi\epsilon_0} \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \cdot \frac{1}{2a} \quad (8)$$

$$\lambda_{R/P}^{o,PT} = \frac{1}{4\pi\epsilon_0} \left[\left(\frac{\epsilon_s - 1}{2\epsilon_s + 1} \right) - \left(\frac{\epsilon_{op} - 1}{2\epsilon_{op} + 1} \right) \right] \cdot \frac{(\mu_R - \mu_P)^2}{a^3} \quad (9)$$

Where a denotes the radius of sphere related to reactant which is not adsorbed on metal slab model. The calculation of radius using Gaussian 09 package.⁷ e_0 denotes elementary charge. Water was chosen as the solvent with dielectric constant of $\epsilon_0 = 8.85 \times 10^{-12}$ (vacuum dielectric constant), $\epsilon_s = 78.4$ (electrostatic dielectric constant) and $\epsilon_{op} = 2$ (optical dielectric constant). μ_R and μ_P are the dipole moments of the reactant and product complexes, respectively.

In this work, we only consider electrochemical nitrogen reduction reaction (NRR) is a concerted proton-electron transfer (CPET) reaction. According to our previous work, a displaced-distorted oscillator model based on classic Marcus theory is proposed to

describe the systems involved in proton and electron transfer. The activation barrier of a concerted proton–electron transfer process is expressed as the following equation:⁸

$$E_{af} = \left(\frac{-\sqrt{\lambda_R} + \sqrt{\frac{\lambda_R}{\lambda_P} \left[\lambda_R + \Delta G \left(\frac{\lambda_R}{\lambda_P} - 1 \right) \right]}}{\lambda_P} \right)^2 \quad (10)$$

$$E_{ab} = \left(\frac{-\sqrt{\lambda_P} + \sqrt{\frac{\lambda_P}{\lambda_R} \left[\lambda_P - \Delta G \left(\frac{\lambda_P}{\lambda_R} - 1 \right) \right]}}{\lambda_R} \right)^2 \quad (11)$$

Where λ_R and λ_P represent the total reorganization energy of reactant and product. ΔG is the change of Gibbs free energy.

The computed rate constant is equal to the pre-exponential factor multiplied by the exponential term related to activation energy. The pre-exponential factor is expressed as:

$$A = \frac{|V|^2}{h} \sqrt{\frac{\pi}{k_B T \lambda}} \quad (12)$$

Here, V equals to $0.5k_B T$.

The expression of effective reorganization energy is as follows:

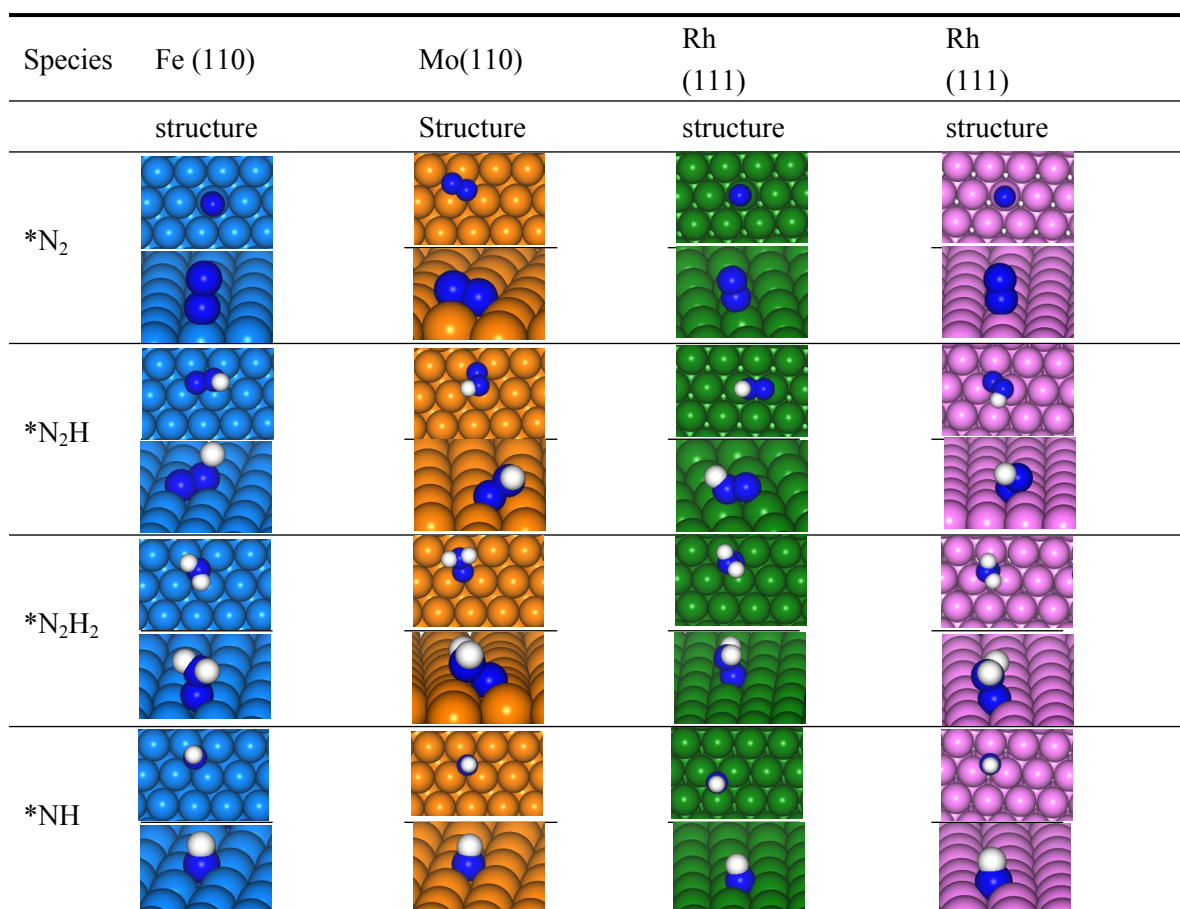
$$\lambda = 4 \left(\frac{\sqrt{\lambda_R} \cdot \sqrt{\lambda_P}}{\sqrt{\lambda_R} + \sqrt{\lambda_P}} \right)^2 \quad (13)$$

The effective reorganization energy is determined by the reorganization energy of both forward and backward reactions.

Table S1. Adsorption energy of adsorbed N₂ and N₂H on Fe(110), Mo(110), Rh(111) and Ru(0001) surfaces by different adsorption patterns. All values are in eV.

Surfaces	Species	Vertical adsorption	Parallel adsorption
Fe(110)	N ₂	-0.38	-0.37
	N ₂ H	-2.33	-2.85
Mo(110)	N ₂	-0.46	-0.75
	N ₂ H	-2.58	-3.67
Rh(111)	N ₂	-0.38	0.20
	N ₂ H	-1.99	-2.12
Ru(0001)	N ₂	-0.45	0.33
	N ₂ H	-2.13	-2.40

Table S2. Top view and front view of the optimized structures of key adsorbates on Fe (110), Mo (110), Rh (111) and Ru (0001) crystal facets. N atoms are in dark blue color and H atoms are in white color.



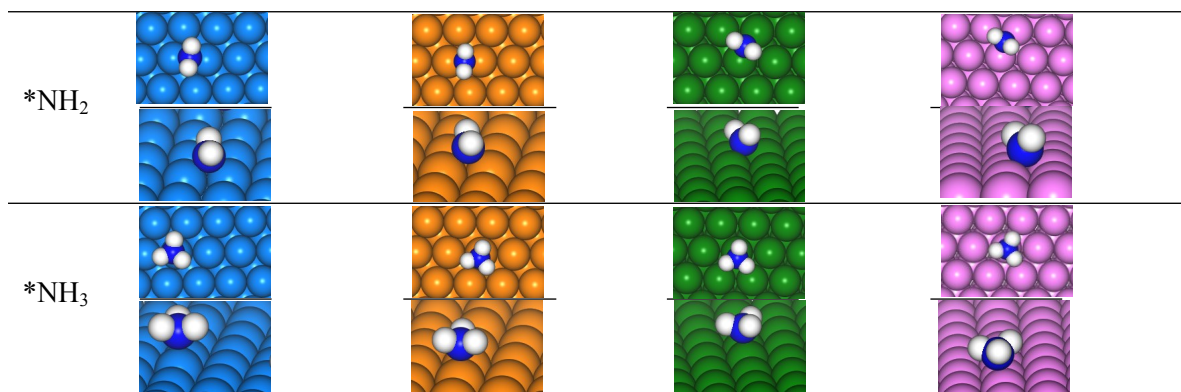


Table S3. Calculated the bond lengths of $*N_2$ and $*N_2H$ on Fe (110), Mo (110), Rh (111) and Ru (0001) crystal facets. N atoms are in dark blue color and H atoms are in white color.

	Free molecule	Fe (110)	Mo (110)	Rh (111)	Ru (0001)
Structure of N_2					
$d_{N-N} / \text{\AA}$	1.12	1.21	1.30	1.14	1.14
Structure of N_2H					
$d_{N-N} / \text{\AA}$	1.20	1.38	1.39	1.25	1.34
$d_{N-H} / \text{\AA}$	1.06	1.03	1.04	1.04	1.04

Table S4. The zero-point energy correction, enthalpy and entropy correction of all possible adsorbates on four metal surfaces. All values are in eV, and all values are calculated at 0 K and 1atm.

Structures	Adsorbate	ZPE	$\int C_p dT - TS$	$ZPE + \int C_p dT - TS$
	$*N_2$	0.20	-0.09	0.11
	$*NNH$	0.45	-0.08	0.37
	$*NNH_2$	0.79	-0.09	0.70

	*N	0.08	-0.01	0.07
	*NH	0.37	-0.03	0.34
	*NH ₂	0.67	-0.04	0.63
	*NH ₃	1.01	-0.11	0.90
	*NHNH	0.81	-0.04	0.77
	*NHNH ₂	1.12	-0.09	1.03
	*NH ₂ NH ₂	1.46	-0.11	1.35
	*N ₂	0.17	-0.04	0.13
	*NNH	0.48	-0.04	0.44
	*NNH ₂	0.85	-0.04	0.81
	*N	0.07	-0.02	0.05
Mo(110)	*NH	0.36	-0.02	0.34
	*NH ₂	0.69	-0.03	0.66
	*NH ₃	1.01	-0.06	0.95
	*NHNH	0.63	-0.10	0.53
	*NHNH ₂	1.18	-0.04	1.14
	*NH ₂ NH ₂	1.47	-0.14	1.33
	*N ₂	0.21	-0.08	0.13
	*NNH	0.49	-0.07	0.42
	*NNH ₂	0.81	-0.07	0.74
	*N	0.09	-0.01	0.08
Rh(111)	*NH	0.38	-0.01	0.37
	*NH ₂	0.70	-0.03	0.67
	*NH ₃	1.02	-0.05	0.97
	*NHNH	0.82	-0.11	0.71
	*NHNH ₂	1.14	-0.08	1.06
	*NH ₂ NH ₂	1.48	-0.14	1.34
	*N ₂	0.21	-0.08	0.13 □
	*NNH	0.49	-0.04	0.45
	*NNH ₂	0.80	-0.05	0.75
	*N	0.09	-0.01	0.08
Ru(0001)	*NH	0.38	-0.01	0.37
	*NH ₂	0.70	-0.03	0.67
	*NH ₃	1.02	-0.05	0.97
	*NHNH	0.82	-0.06	0.76
	*NHNH ₂	1.13	-0.09	1.04
	*NH ₂ NH ₂	1.48	-0.13	1.35

Table S5. The zero-point energy correction, enthalpy and entropy correction for free modules. All values are given in eV, and all values are calculated at 0 K and 1 atm.

Species	ZPE	$\int C_p dT - TS$	$ZPE + \int C_p dT - TS$
N₂(g)	0.19	-0.53	-0.34
H₂(g)	0.29	-0.33	-0.04
NH₃	0.91	-0.50	0.41

Table S6. Calculated internal reorganization energy, solvent reorganization energy related to electron transfer, and solvent reorganization energy related to proton transfer for CPET process of electrochemical NRR on four metal surfaces. All values are given in eV.

CPET process	Metal surfaces	λ_R	λ_P	λ_R^i	λ_P^i	$\lambda_R^{o,ET}$	$\lambda_P^{o,ET}$	$\lambda_R^{o,PT}$	$\lambda_P^{o,PT}$
*N ₂ +H ⁺ +e ⁻ → *NNH	Fe(110)	1.47	2.52	0.18	1.21	1.24	1.26	0.05	0.05
	Mo(110)	1.31	1.97	0.03	0.66	1.24	1.26	0.05	0.05
	Rh(111)	2.12	2.13	0.82	0.82	1.24	1.26	0.05	0.05
	Ru(0001)	2.40	2.22	1.10	0.90	1.24	1.26	0.05	0.05
*NNH+H ⁺ +e ⁻ →*NNH ₂	Fe(110)	2.05	2.90	0.75	1.69	1.26	1.18	0.04	0.03
	Mo(110)	1.90	2.71	0.75	1.69	1.26	1.18	0.04	0.03
	Rh(111)	1.79	3.82	0.49	2.60	1.26	1.18	0.04	0.03
	Ru(0001)	1.80	4.74	0.51	3.53	1.26	1.18	0.04	0.03
*NNH ₂ +H ⁺ +e ⁻ →*N+NH ₃	Fe(110)	2.27	2.98	1.05	1.79	1.18	1.15	0.05	0.05
	Mo(110)	2.83	5.53	1.60	4.34	1.18	1.15	0.05	0.05

	Rh(111)	3.33	2.53	2.10	1.33				
						1.18	1.15	0.05	0.05
	Ru(0001)	2.93	2.76	1.71	1.56				
*N+H ⁺ +e ⁻ →*NH	Fe(110)	1.74	2.19	0.33	0.82	1.36	1.33	0.04	0.04
	Mo(110)	1.58	1.60	0.17	0.22	1.36	1.33	0.04	0.04
	Rh(111)	1.61	1.57	0.21	0.20	1.36	1.33	0.04	0.04
	Ru(0001)	1.58	1.58	0.17	0.21	1.36	1.33	0.04	0.04
*NH+H ⁺ +e ⁻ →*NH ₂	Fe(110)	2.50	2.31	1.16	1.02	1.33	1.29	0.00	0.00
	Mo(110)	2.54	2.48	1.20	1.19	1.33	1.29	0.00	0.00
	Rh(111)	2.32	2.69	0.99	1.40	1.33	1.29	0.00	0.00
	Ru(0001)	2.60	3.32	1.26	2.02	1.33	1.29	0.00	0.00
*NH ₂ +H ⁺ +e ⁻ → *NH ₃	Fe(110)	2.18	2.41	0.88	1.14	1.29	1.27	0.00	0.00
	Mo(110)	2.41	2.43	1.12	1.17	1.29	1.27	0.00	0.00
	Rh(111)	2.09	3.00	0.79	1.73	1.29	1.27	0.00	0.00
	Ru(0001)	2.19	3.72	0.90	2.45	1.29	1.27	0.00	0.00
*NNH+H ⁺ +e ⁻ →*NHNH	Fe(110)	2.04	1.94	0.76	0.76	1.26	1.16	0.01	0.01
	Mo(110)	1.90	2.04	0.62	0.87	1.26	1.16	0.01	0.01
	Rh(111)	1.68	1.40	0.41	0.23	1.26	1.16	0.01	0.01
	Ru(0001)	1.62	2.75	0.35	1.57	1.26	1.16	0.01	0.01
*NHNH+H ⁺ +e ⁻ →*NHNH ₂	Fe(110)	2.81	1.69	1.65	0.56	1.16	1.13	0.00	0.00
	Mo(110)	2.07	3.30	0.91	2.17	1.16	1.13	0.00	0.00
	Rh(111)	2.05	1.32	0.89	0.19	1.16	1.13	0.00	0.00
	Ru(0001)	2.57	2.61	1.41	1.48	1.16	1.13	0.00	0.00

*NNH ₂ +H ⁺ +e ⁻	Fe(110)	2.39	2.61	1.21	1.47	1.18	1.13	0.01	0.01
→*NHNH ₂									
	Mo(110)	1.99	2.25	0.83	1.11	1.18	1.13	0.01	0.01
	Rh(111)	1.19	3.10	1.02	1.97	1.18	1.13	0.01	0.01
	Ru(0001)	2.19	3.72	0.90	2.45	1.18	1.13	0.01	0.01

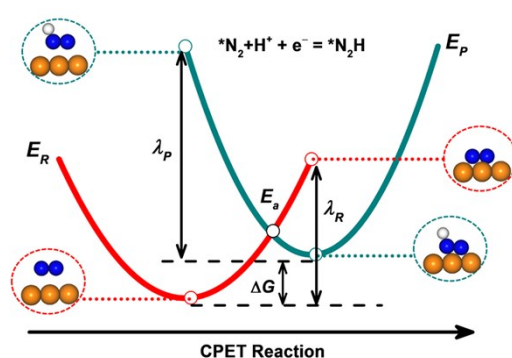


Figure S1. Potential energy curves for $*N_2$ (E_R , red) and $*N_2H$ (E_P , green) for the CPET process of $*N_2 + H^+ + e^- \rightarrow *N_2H$. The geometry modifications of $*N_2$ and $*N_2H$ from the equilibrium configuration of reactant to product are given above.

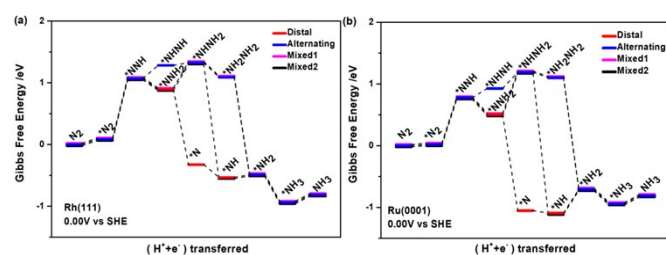


Figure S2. Gibbs free energy diagram for NRR on Rh (111) and Ru (0001) through four possible mechanism at 0 V.

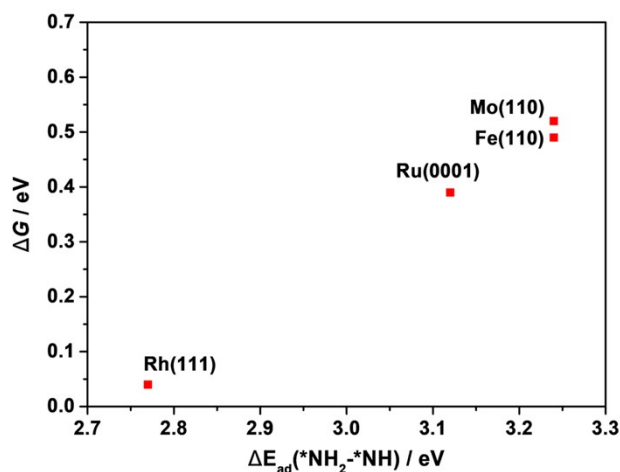


Figure S3. Relationships between ΔG and adsorption energy difference of $*\text{NH}_2$ and $*\text{NH}$ on on four metal surfaces.

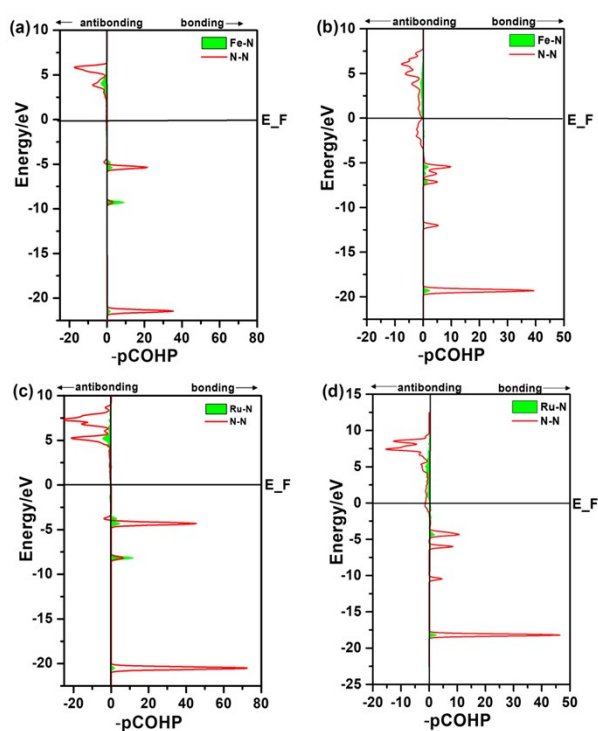


Figure S4. (a) Projected crystal orbital Hamilton populations ($-\text{pCOHP}$) of N-N bonds and the N-Fe bonds after the adsorption of N_2 on Fe(110) (b) Projected crystal orbital Hamilton populations ($-\text{pCOHP}$) of N-N bonds and the N-Fe bonds after the adsorption of NNH on Fe(110). (c) Projected crystal orbital Hamilton populations ($-\text{pCOHP}$) of N-N bonds and the N-Ru bonds after the adsorption of N_2 on Ru(0001) (d) Projected

crystal orbital Hamilton populations ($-p\text{COHP}$) of N-N bonds and the N-Ru bonds after the adsorption of NNH on Ru(0001).

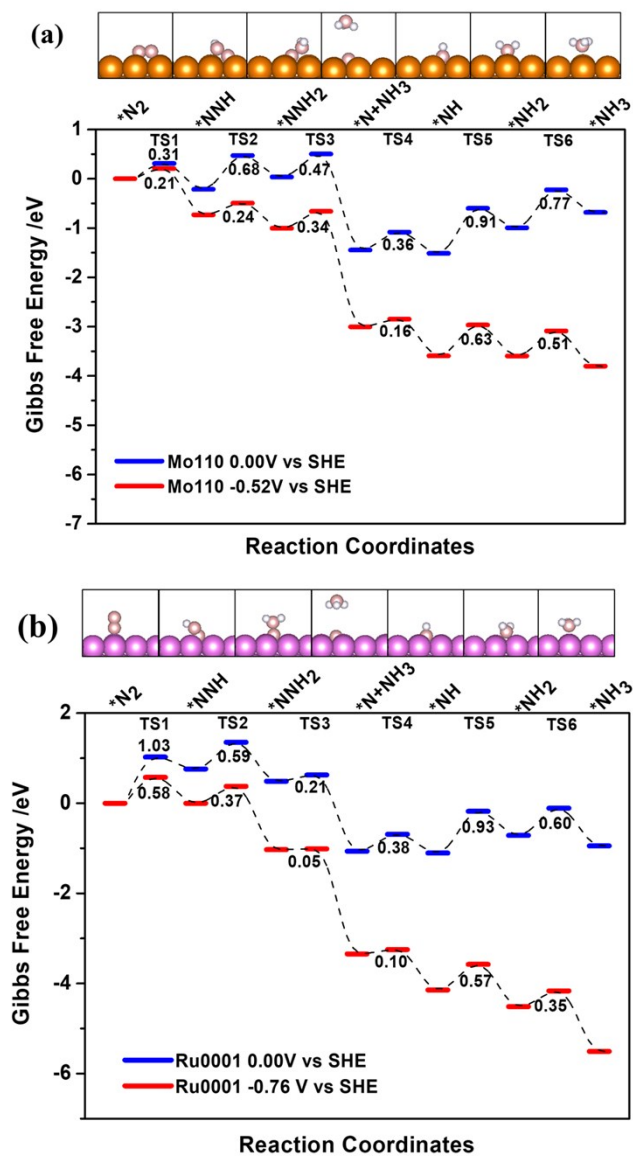


Figure S5. (a) Potential energy curves of Mo(110) at 0 V and -0.52 V. (b) Potential energy curves of Ru(0001) at 0 V and -0.76 V.

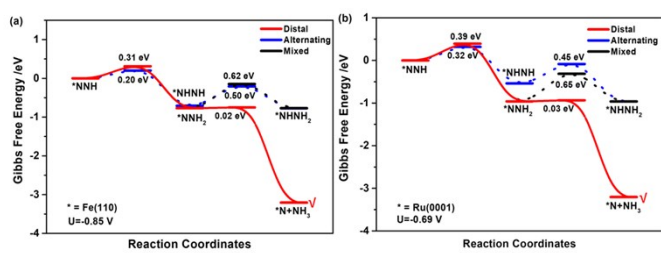


Figure S6. (a) Potential energy curves of competitive reactions of four reaction mechanisms on Fe(110) at -0.85 V (b) Potential energy curves of competitive reactions of four reaction mechanisms on Ru(0001) at -0.69 V

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