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Supplementary information

Reaction mechanism and kinetics for N₂ reduction to ammonia on Fe-Ru dual atom catalyst

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Supplementary information details GCP Formulation Table S1-S2 Figures S1-S21

GCP Formulation:

The derivation grand canonical potential kinetics starts with the definition of grand canonical potential, which is defined as;

$$G(n, U) = F(n) + ne(U_{SHE} - U)$$
⁽¹⁾

Here G is the grand canonical free energy, which depends on the number of electrons (n), the applied potential (U vs SHE), total free energy (F) as a function of (n), and electronic energy (U_{SHE} = $\mu_{e,SHE}/e$) at the standard hydrogen electrode (SHE) condition. Optimizing the number of electrons for each U, we obtain the GCP (U) as follows,

$$\frac{dG(n;U)}{dn} = 0 \quad or \quad \mu_e = \frac{dF(n)}{dn} = e \left(U_{SHE} - U \right)$$
(2)

$$GCP(U) = \min G(n;U) = \min \left\{ F(n) - ne(U_{SHE} - U) \right\}$$
(3)

Approximating F(n) locally as quadratic and minimizing G(n;U) leads to a quadratic form in GCP(U). To obtain or GCP(U), we fit a quadratic expansion of F(n):

$$F(n) = a (n - n_0)^2 + b (n - n_0) + c$$
(4)

where a, b, and c are determined from the QM calculations. Minimization of (4) (Supplementary Table 1-5) leads to equation (5).

$$GCP(U) = -\frac{1}{4a}(b - \mu_{e,SHE} + eU)^2 + c - n_0\mu_{e,SHE} + n_0eU$$
(5)

These parameters are related to physical quantities as follows,

First, the differential capacitance, $C_{diff} = \frac{\partial n}{\partial U} = \frac{1}{2a}$ which lead as to $a = -\frac{1}{2C_{diff}}$

Second, at the potential of zero charge, $n(U_{PZC}) = n_0$, so we obtain

$$n(U) = -\frac{1}{e} \frac{\partial GCP(U)}{\partial U} = n_0 - \frac{1}{2ae} (b - \mu_{e,SHE} + eU),$$

Thus, we can write, $b = \mu_{e,SHE} - eU_{PZC}$

Finally, $F(n = n_0) = c$, when the system is neutral, the potential of zero charge (U_{PZC})

Putting these physical quantities into equations (4) and (5) we write the grand canonical potential and free energy expressions as in (6) and (7)

$$F(n) = -\frac{1}{2C_{diff}} (n - n_0)^2 + (\mu_{e,SHE} - eU_{PZC})(n - n_0) + F_0 \qquad (6)$$
$$GCP(U) = \frac{e^2 C_{diff}}{2} (U - U_{PZC})^2 + n_0 eU + F_0 - n_0 \mu_{e,SHE} \qquad (7)$$

Species	a = -1	$b = \mu_{e,SHE} - eU_{PZC}$	c = Fo	Vibrational
	2C _{diff}	(eV/electron)	(eV)	contribution
	(eV/electron ²)			(kcal/mol)
N ₂	0.25	-4.27	-16485.20	52.45
N ₂ H	0.16	-4.25	-16500.69	58.77
N ₂ H ₂	0.20	-4.14	-16516.86	65.83
N ₂ H ₃	0.23	-4.04	-16532.33	67.71
N	0.22	-4.35	-16213.36	50.25
NH	0.22	-4.27	-16229.56	54.39
NH ₂	0.22	-4.21	-16246.18	63.26
NH ₃	0.22	-4.09	-16261.64	69.67
TS ab	0.26	-4.12	-17910.16	48.13
TS cd	0.20	-4.06	-17941.90	65.54
TS de	0.27	-4.14	-16532.25	24.45
TS ef	0.20	-4.10	-17638.56	47.55
TS gh	0.26	-4.01	-17670.95	61.15
TS hi	0.19	-3.84	-17685.94	70.34
Н	0.19	-4.16	-15957.35	53.27
H ₂	0.25	-4.35	-17382.69	56.33
H ₃	0.24	-4.22	-15989.016	58.15
TS ai	0.21	-4.05	-17366.289	45.19
TS ij	0.27	-4.14	-17382.53	50.48
TS jk	0.44	-4.05	-17398.346	51.36

 Table S1: parameters obtained from quadratic fitting to obtain the grand canonical potential

Reaction step	Applied potential	TS - IS	FS - TS	Total charge
	U vs RHE			transfer
Step ab	0	0.34	0.18	0.54
$N_2 \rightarrow N_2 H$	-0.2	0.30	0.18	0.50
Step cd	0	0.25	0.08	0.33
$N_2H_2 \rightarrow N_2H_3$	-0.2	0.24	0.02	0.26
Step ef	0	0.04	0.41	0.45
$N \rightarrow NH$	-0.2	0.08	0.28	0.36
Step gh	0	0.18	0.05	0.23
$NH_2 \rightarrow NH_3$	-0.2	0.19	0.04	0.23
Step ha NH ₃ \rightarrow NH ₄ ⁺	0	0.15	0.00	0.15
	-0.2	0.15	0.00	0.15
Step ai	0	0.23	0.42	0.65
$* \rightarrow *H$	-0.2	0.19	0.43	0.62
Step ij	0	0.46	0.38	0.84
$*H \rightarrow *H_2$	-0.2	0.34	0.41	0.78
Step jk	0	0.51	0.21	0.72
$*H_2 \rightarrow *H_3$	-0.2	0.15	0.36	0.51

Table S2: Charge variation as a function of applied potential.

IS = Initial state, TS = transition state, FS = Final state



Figure S1: NRR reaction mechanism (a) Associative pathway, and (b) Enzymatic pathway



Reaction pathway

Figure S2: Free energy profile of NRR via associative pathway as a function of applied potential



Figure S3: Optimized structures of reaction intermediates for NRR associative pathway on Fe-Ru surface



Figure S4: Alternating pathway vs distal pathway for NRR



Figure S5: Free energy profile of NRR via enzymatic pathway as a function of applied potential



Figure S6: Optimized structures of reaction intermediates of the NRR enzymatic pathway



Figure S7: Behavior of free energy and grand canonical potential as a function of number of electrons. a. The free energies as a function of electrons show a linear relationship. **b**. the relation between free energy and number of electrons becomes quadratic when the energy contribution of each electron at SHE is subtracted from the total free energy. **c.** Minimization of free energy as a function of number of electron when an external potential is applied to the system.



Figure S8: (a) CI-NEB path for the conversion of N_2 to N_2H , (b) Energy profile for the reaction pathway



Figure S9: (a) CI-NEB path for the conversion of N_2H to N_2H_2 , **(b)** Energy profile for the reaction pathway



Figure S10: (a) CI-NEB path for the conversion of N_2H_2 to N_2H_3 , (b) Energy profile for the reaction pathway



Figure S11: (a) CI-NEB path for the conversion of N_2H_3 to $N + NH_3$, **(b)** Energy profile for the reaction pathway.



Figure S12: (a) CI-NEB path for the conversion of *N to *NH, **(b)** Energy profile for the reaction pathway.



Figure S13: (a) CI-NEB path for the conversion of $*NH_2$ to $*NH_3$, (b) Energy profile for the reaction pathway.



Figure S14: (a) CI-NEB path for the conversion of $*NH_3$ to NH_4^+ , **(b)** Energy profile for the reaction pathway



Figure S15: (a) CI-NEB path for the conversion of $*N_2$ to $*N_2H$ for enzymatic pathway (b) Energy profile for the reaction pathway.



Figure S16: (a) CI-NEB path for the conversion of $*N_2H$ to $*N_2H_2$ for enzymatic pathway, **(b)** Energy profile for the reaction pathway.



Figure S17: (a) CI-NEB path for the conversion of $*N_2H_2$ to $*N_2H_3$ for enzymatic pathway, (b) Energy profile for the reaction pathway.



Figure S18: (a) CI-NEB path for the conversion of $*N_2H_2$ to *NH + *NH for enzymatic pathway, (b) Energy profile for the reaction pathway.



Figure S19: (a) CI-NEB path for the conversion of 1st Volmer step, **(b)** Energy profile for the reaction pathway.



Figure S20: (a) CI-NEB path for the conversion of 2nd Volmer step, **(b)** Energy profile for the reaction pathway.



Figure S21: (a) CI-NEB path for the conversion of 3rd Volmer step, **(b)** Energy profile for the reaction pathway.

Current density calculations

Density of [Fe-Ru] (7.1428%) = 2.73×10^{16} atoms/cm²

Current density, j (mA/cm²) = n * F * r_{NH3} *1000

Where, n = number of electrons transferred in volved in the reaction (for NH₃, n=6),

F = Faraday's constant

 r_{NH3} = reaction rate of NH₃

For Turn over frequency (TOF) Calculation

TOF = TON/Number of active sites

For Turn over number (TON) = $(J(A) * t * FE_{NH3})/2F$