Supplementary information for:

Electrocatalytic oxidation of Ammonia on Transition Metal Surfaces: A First-Principles Study

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S1. Optimized geometries of adsorbates

Figures S1-4 show the optimized structures of adsorbed H_xNNH_y intermediates on Re(0001),

Ru(0001), Os(0001), Co(0001), Rh(111), Ir(111), Ni(111), Pd(111), Cu(111), Ag(111), and

Au(111).

Re(0001) NNH HNNH NNH₂ HNNH₂ H₂NNH₂ Ru(0001) H₂NNH₂ NNH HNNH NNH₂ HNNH₂ Os(0001) HNNH NNH₂ HNNH₂ H₂NNH₂ NNH

Figure S1. Optimized geometries of H_xNNH_y species in their minimum energy structures on Re(0001), Ru(0001), and Os(0001). Images show overhead view (above) and side view (below).

Co(0001)



NNH













HNNH₂

H₂NNH₂













Rh(111)









HNNH₂



NNH











lr(111)



NNH







HNNH₂

 H_2NNH_2



Figure S2. Optimized geometries of H_xNNH_y species in their minimum energy structures on Co(0001), Rh(111), and Ir(111). Images show overhead view (above) and side view (below).



Figure S3. Optimized geometries of H_xNNH_y species in their minimum energy structures on Ni(111) and Pd(111). Images show overhead view (above) and side view (below).

Cu(111)



NNH





NNH₂







HNNH₂





Ag(111)









NNH











Au(111)











HNNH₂ H₂NNH₂

Figure S4. Optimized geometries of H_xNNH_y species in their minimum energy structures on Cu(111), Ag(111), and Au(111). Images show overhead view (above) and side view (below).

S2. Free energy diagrams

Figures S5-S14 show free energy diagrams of NH₃ electro-oxidation for Re(0001), Ru(0001),



Os(0001), Co(0001), Rh(111), Ir(111), Ni(111), Pd(111), Ag(111), and Au(111).

Reaction Coordinate

Figure S5. Free energy diagram for ammonia electro-oxidation on Re(0001) at 0 V_{RHE} . Stoichiometry is balanced with OH⁻, H₂O, H₊, and e⁻, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).



Reaction Coordinate

Figure S6. Free energy diagram for ammonia electro-oxidation on Ru(0001) at 0 V_{RHE}. Stoichiometry is balanced with OH⁻, H₂O, H₊, and e⁻, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).



Figure S7. Free energy diagram for ammonia electro-oxidation on Os(0001) at 0 V_{RHE} . Stoichiometry is balanced with OH⁺, H₂O, H+, and e⁻, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).



Figure S8. Free energy diagram for ammonia electro-oxidation on Co(0001) at 0 V_{RHE}. In purple and red are N-N bond formation reaction steps with the respective transition state (TS) energies. Stoichiometry is balanced with OH⁻, H₂O, H+, and e⁻, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).



Figure S9. Free energy diagram for ammonia electro-oxidation on Rh(111) at 0 V_{RHE} . In purple and red are N-N bond formation reaction steps with the respective transition state (TS) energies. Stoichiometry is balanced with OH⁻, H₂O, H+, and e⁻, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).



Figure S10. Free energy diagram for ammonia electro-oxidation on Ir(111) at 0 V_{RHE}. In purple and red are N-N bond formation reaction steps with the respective transition state (TS) energies. Stoichiometry is balanced with OH⁻, H₂O, H+, and e⁻, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).



Figure S11. Free energy diagram for ammonia electro-oxidation on Ni(111) at 0 V_{RHE}. Stoichiometry is balanced with OH⁻, H₂O, H₊, and e⁻, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).



Figure S12. Free energy diagram for ammonia electro-oxidation on Pd(111) at 0 V_{RHE} . In purple and red are N-N bond formation reaction steps with the respective transition state (TS) energies. Stoichiometry is balanced with OH⁻, H₂O, H+, and e⁻, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).



Figure S13. Free energy diagram for ammonia electro-oxidation on Ag(111) at 0 V_{RHE}. Stoichiometry is balanced with OH⁺, H₂O, H₊, and e⁺, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).



Figure S14. Free energy diagram for ammonia electro-oxidation on Au(111) at 0 V_{RHE} . Stoichiometry is balanced with OH⁻, H₂O, H₊, and e⁻, which are not shown explicitly. All energies are given with adsorbates at infinite separation, 1/9 ML coverage. Zero energy corresponds to N₂(g).