

# Supplementary Information for “On the Mechanism of Electrochemical Ammonia Synthesis on the Ru Catalyst”

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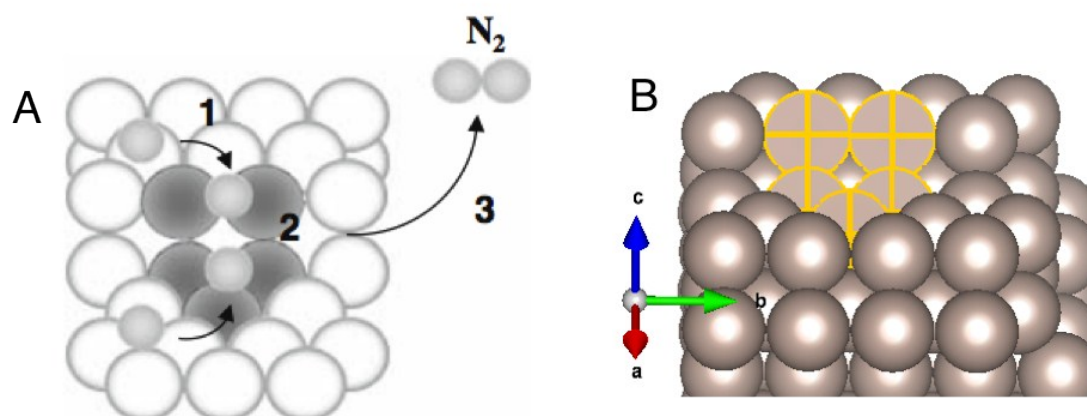
**Table S1.** Correction terms (zero-point energy, enthalpic temperature, entropy corrections) of adsorbates used to convert electronic energies into free energies. Displacement of adsorbate atoms is limited to  $\pm 0.01$  Å and temperature is set to 298.15 K.

Adsorbates	ZPE (eV)	$\int C_p dT$	-TS	ZPE + $\int C_p dT$ - TS
*N <sub>2</sub> H <sub>2</sub>	0.78	0.08	-0.16	-0.16
*N <sub>2</sub> H	0.48	0.07	-0.13	-0.13
*N <sub>2</sub>	0.20	0.08	-0.18	-0.18
*NH <sub>2</sub>	0.69	0.05	-0.09	-0.09
*NHNH	0.79	0.08	-0.15	-0.15
*NH	0.379	0.028	-0.039	-0.039
*N	0.093	0.018	-0.026	-0.026
*NH <sub>2</sub> NH	1.11	0.08	-0.15	-0.15
*NH <sub>2</sub> NH	1.46	0.062	-0.103	-0.103
*H	0.16	0.01	-0.02	-0.02

**Table S2.** Correction terms (zero-point energy, enthalpic temperature, entropy corrections) of gas-phase molecules used to convert electronic energies into free energies. Partial pressure and temperature are set to 101325 Pa and 298.15 K, respectively.

Adsorbates	ZPE (eV)	$\int C_p dT$	$-TS$	$ZPE + \int C_p dT - TS$
H <sub>2</sub>	0.26	0.09	-0.40	-0.06
N <sub>2</sub>	0.15	0.09	-0.59	-0.36
NH <sub>3</sub>	0.97	0.11	-0.60	0.48
N <sub>2</sub> H <sub>2</sub>	0.76	0.10	-0.68	0.19
N <sub>2</sub> H <sub>4</sub>	1.37	0.11	-0.71	0.77

**Figure S1.** Comparison of (A) the B5-type site and (B) the supercell used in the present study. The current supercell contains the B5-type active site of the conventional Haber-Bosch process as well as the edge sites.



(A) B5-type site (Top Catal (2009) 52:758–764), (B) a supercell used in our work (repeated by 2 times in x-axis)