Supporting Information

Deciphering the Dynamic Behavior of Geminal-Cu Sites for High-Efficient Nitrate Reduction to Ammonia

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Computed Gibbs free energy of NO_3^-

The Gibbs free energy change for the adsorption of aqueous nitrate onto the electrode surface (NO_3^-(l) to forming *NO_3) was calculated using a thermodynamic cycle[1,2] that employs HNO_3(g) as a reference, according to the following three steps:

$$HNO_3(g) + * \rightarrow HNO_3(l) + * \quad (S1)$$

$$HNO_3(l) + * \rightarrow H^+ + NO_3^-(l) + * \quad (S2)$$

$$NO_3^- + * \rightarrow *NO_3 + e^- \quad (S3)$$

therefore, the adsorption of nitrate as described below，

$$HNO_3(g) + * \rightarrow *NO_3 + 1/2H_2(g) \quad (S4)$$

the adsorption Gibbs free energy of NO_3^- referenced to HNO_3(g), estimated as:

$$\Delta G_{ads}(*NO_3) = G_{*NO3} - (E_{Cug/PCN} + G_{gas}(HNO_3) - 1/2G_{H2}) \quad (S5)$$

where G_{*NO3}, $G_{gas}(HNO_3)$, and G_{H2} are all calculated using the relation $G = E + (\Delta H - T\Delta S)$, with E, ΔH, and ΔS is electronic energies obtained from DFT calculations, enthalpic and entropic contributions, respectively. All Gibbs free energy calculations were performed at 298.15 K and 1 atm. The ΔG for HNO_3(g) relative to solution is approximately 0.392 eV.[3]

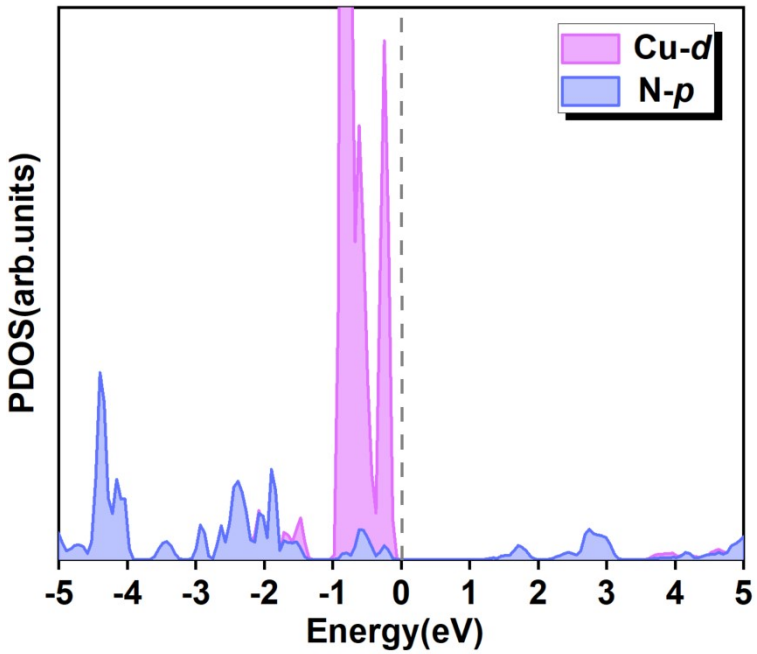


Fig. S1 The PDOS of Cu_g/PCN. The Fermi level (0 eV) is indicated by the gray dashed line.

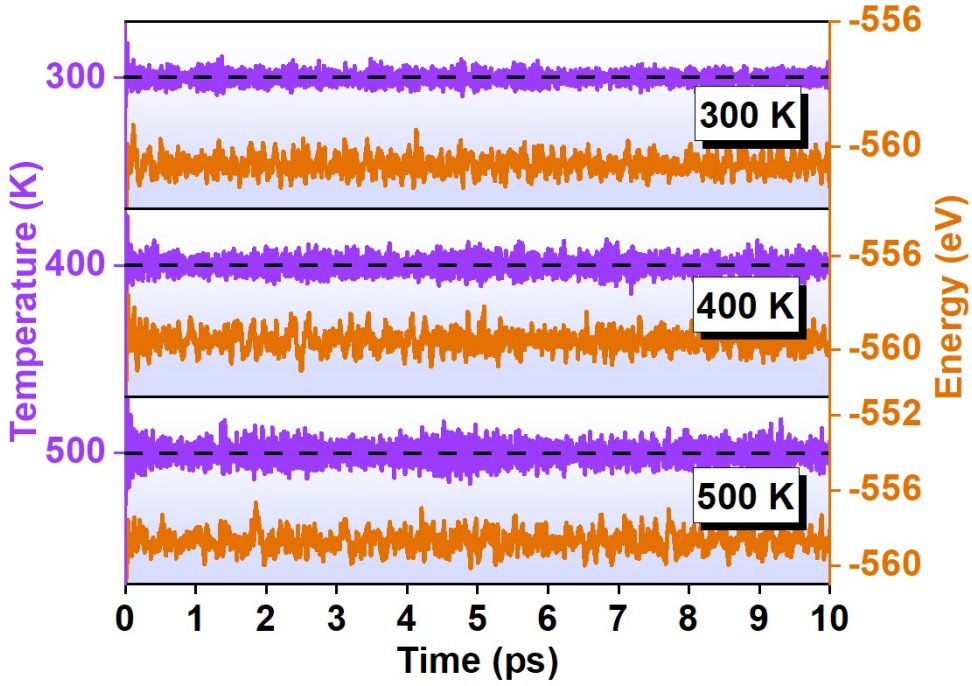


Fig. S2. The AIMD simulations of Cu_g/PCN models were conducted at 300 K, 400 K, and 500 K for 10 ps using a 1fs time step.

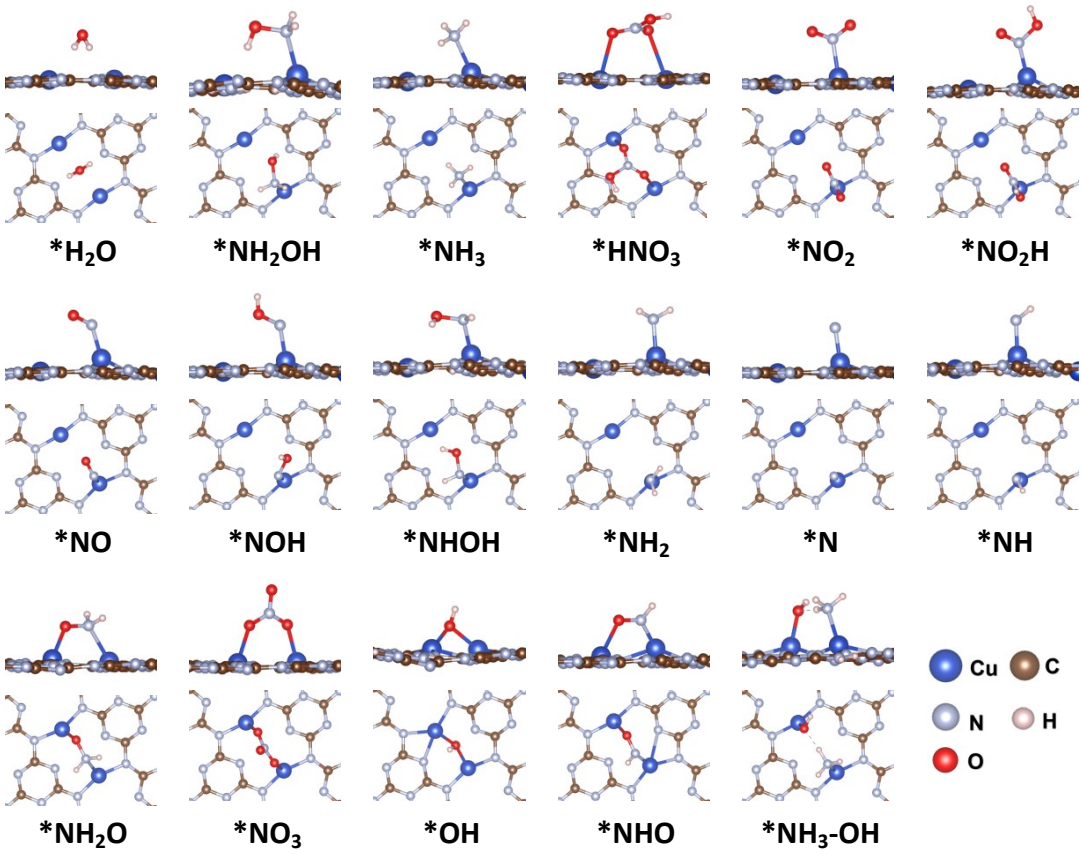


Fig. S3 Optimized structures of all intermediates in the NO_3 reduction mechanism. The blue, gray, red, brown and light pink balls represent Cu, N, O, C and H atoms, respectively.

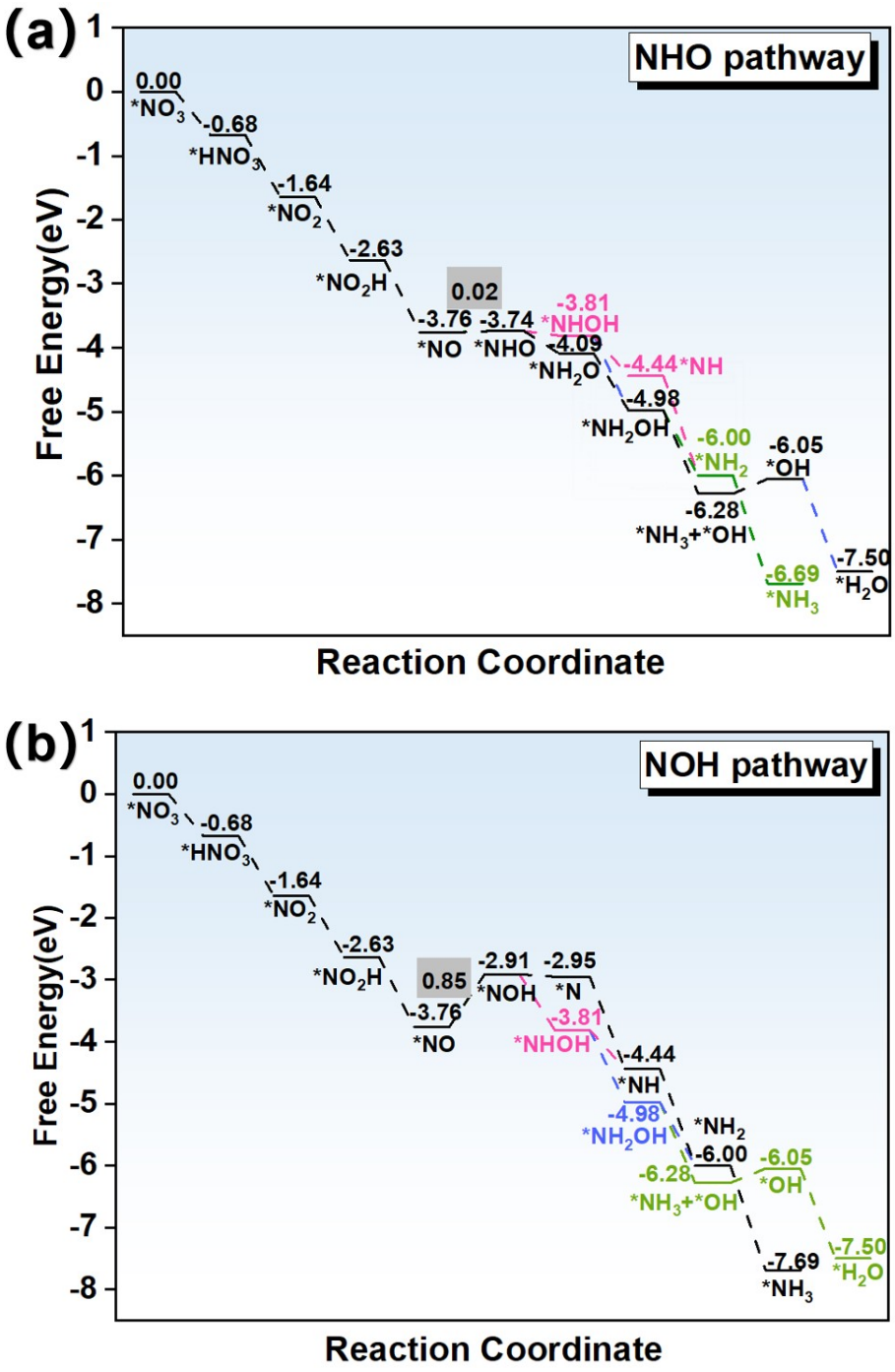
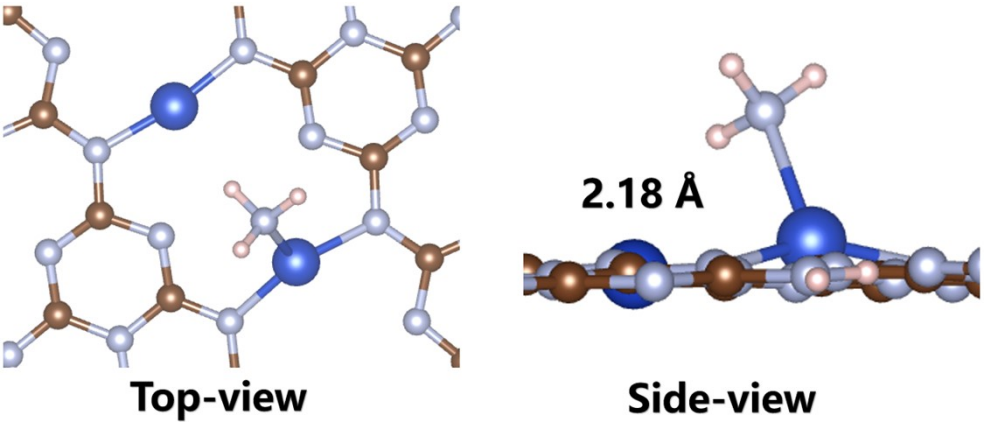


Fig. S4 Free energy diagrams of possible reaction pathways for NO_3RR on Cu_g/PCN (T = 298.15 K, pH = 0). (a) The NHO pathway; (b) the NOH pathway.



$$E_{ads} = -0.38\ eV$$

$$\Delta G_{*NH_3 \rightarrow * + NH_3(g)} = -0.13\ eV$$

Fig. S5 Optimized structure ($d_{Cu\text{-}N}$ = 2.18 Å) and adsorption energy of $*NH_3$ on Cu_g/PCN (compared to E_{ads} = -0.32 eV in reference[4]).

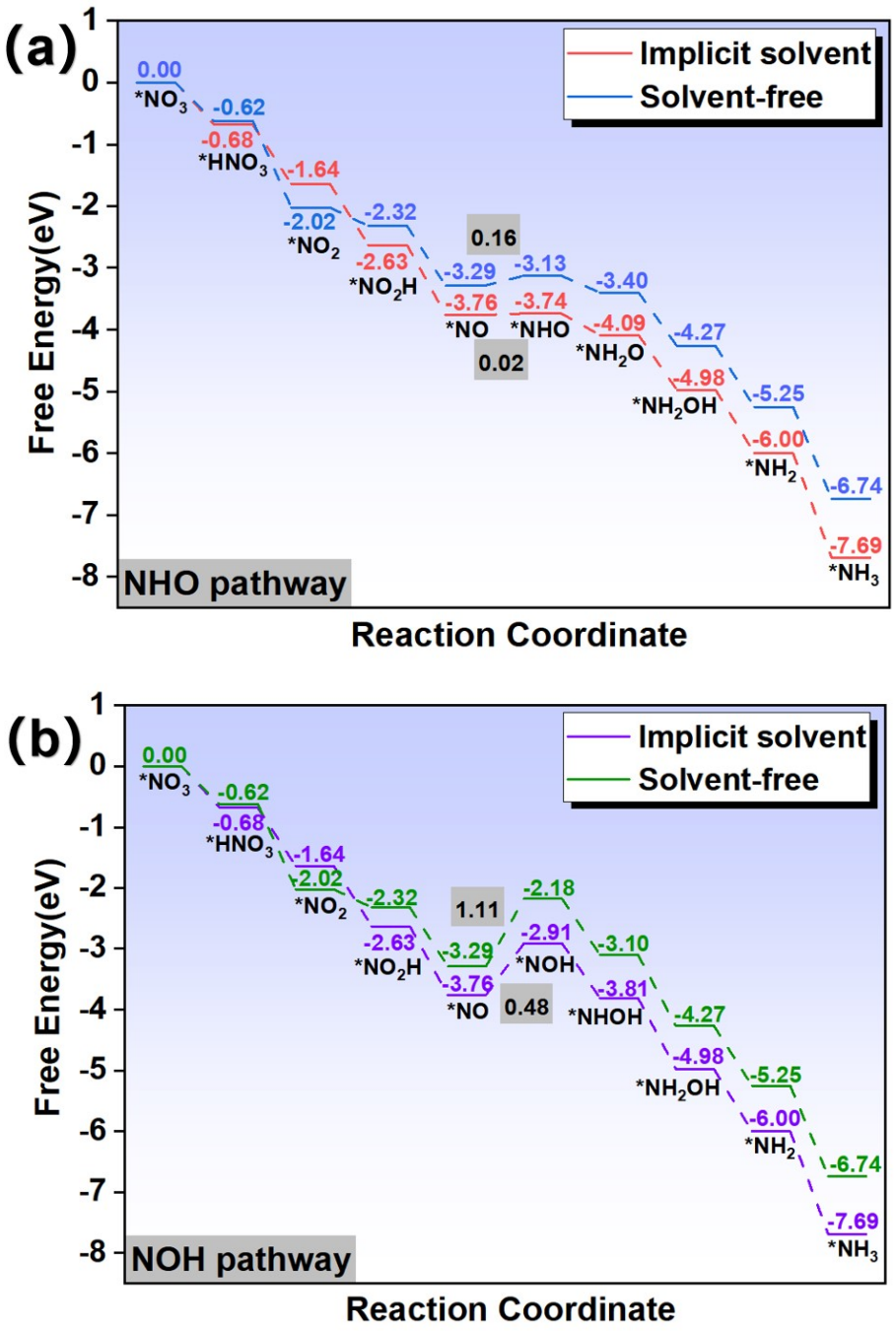


Fig. S6 Comparison of free energy diagrams for NO_3RR under solvent-free and implicit solvent environment (T = 298.15 K, pH = 0). (a) The NHO pathways; (b) the NOH pathways.

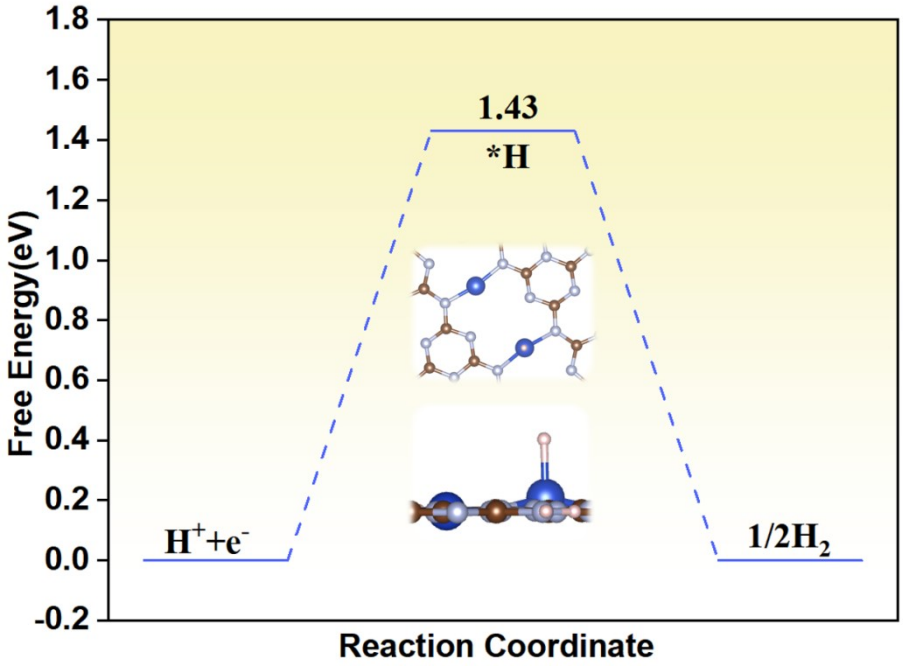


Fig. S7 Free energy profile of the HER catalyzed by Cu_g/PCN (T = 298.15 K, pH = 0).

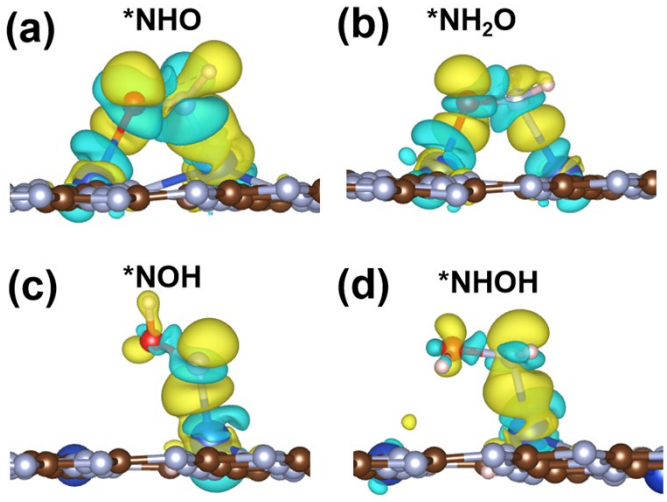


Fig. S8 Charge density difference analysis of key intermediates adsorbed on geminal-Cu sites. (a)*NHO; (b)*NH_2O; (c)*NOH; (d)*NHOH. The isovalue was set to 0.002 eV·$bohr^{-3}$.

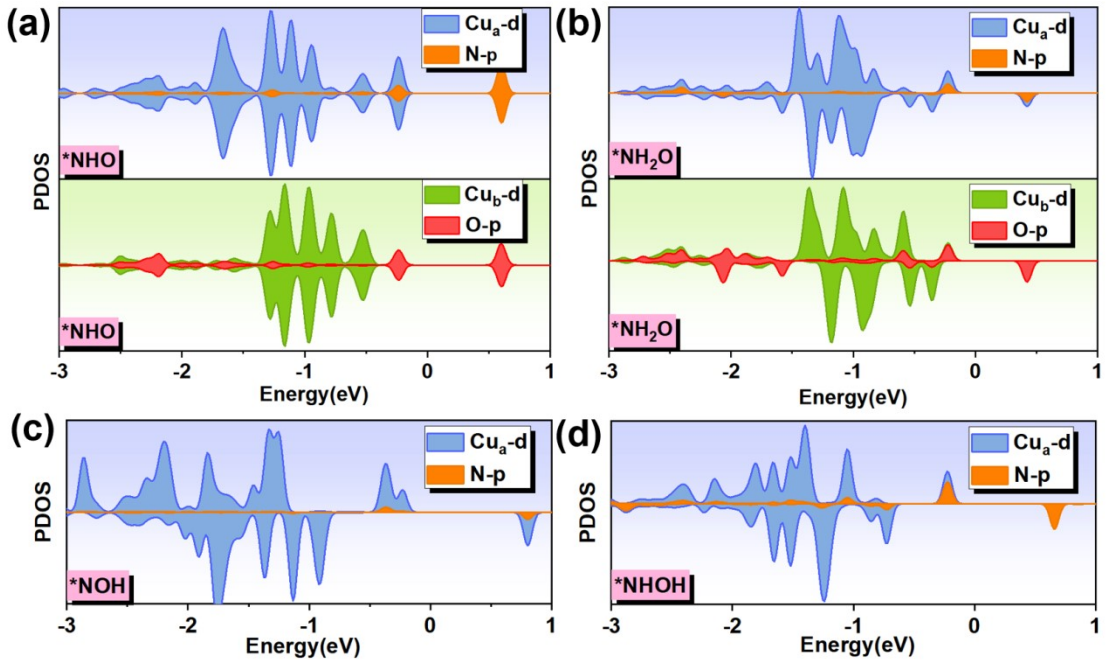


Fig. S9 PDOS analysis of key intermediates adsorbed on geminal-Cu sites. (a)*NHO; (b)*NH_2O; (c)*NOH; (d)*NHOH.

Table S1 Calculated Gibbs free energy, ΔE, ΔE_{ZPE}, ΔS (in eV) of *NH_3 desorbed on Cu_g/PCN (pH=0, T=298.15K).

Cu_g/PCN	ΔE	ΔE_{ZPE}	TΔS	ΔG
*NH_3 → * + NH_3(g)	0.38	-0.09	0.42	-0.13

REFERENCES

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