Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Enhancing the Nitrogen Reduction Activity of Iron with Inactive Group-IVA Elements by Optimized Stoichiometry

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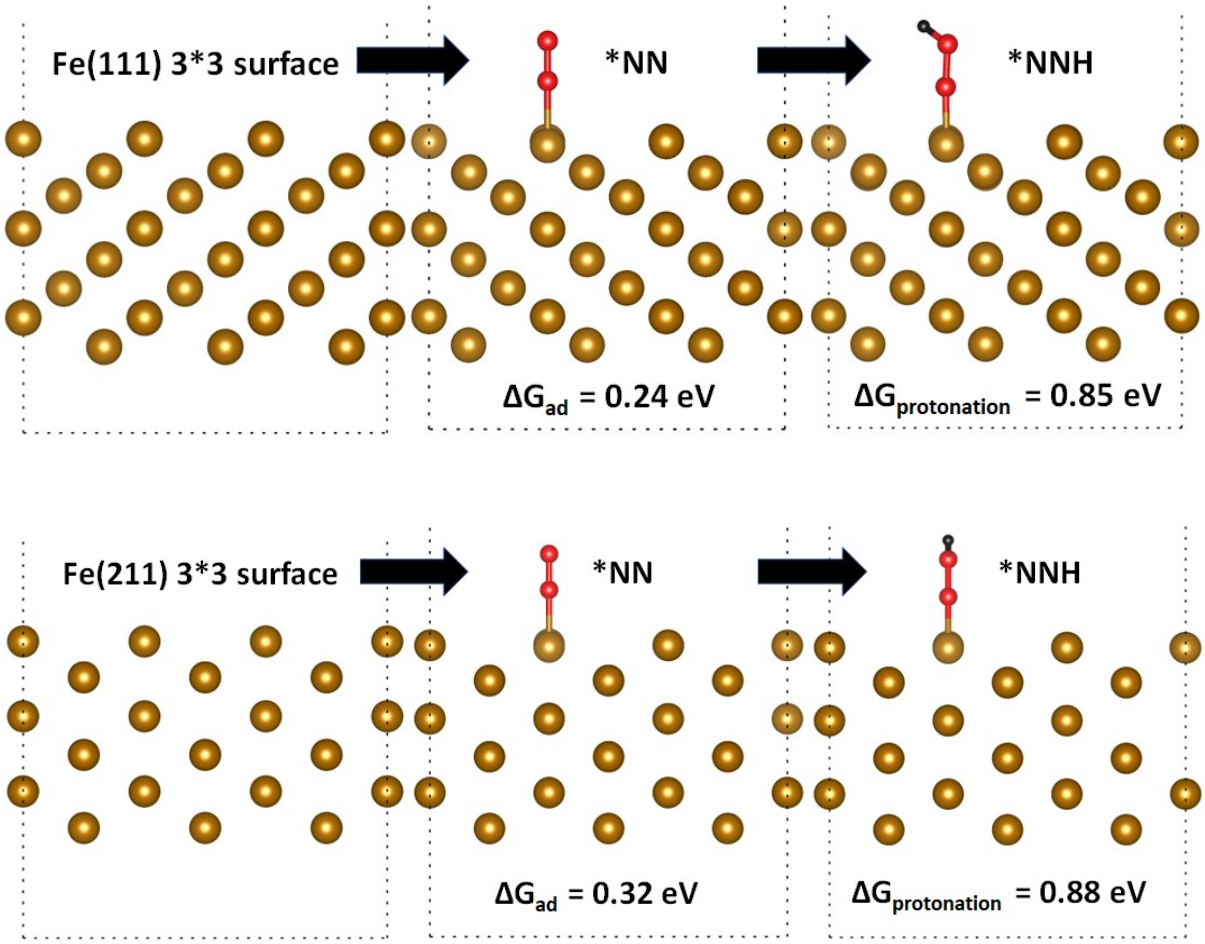

Figure S1: Free energy file of N_2 adsorption and the first hydrogenation step on Fe(111) and Fe(211). Both have a largely positive free energy change of the first hydrogenation step, making them inefficient for e-N2RR. The horizontal adsorption mode is not available due to the large distance between surface iron atoms. Color map: bronze—Fe; red—N; black—H.

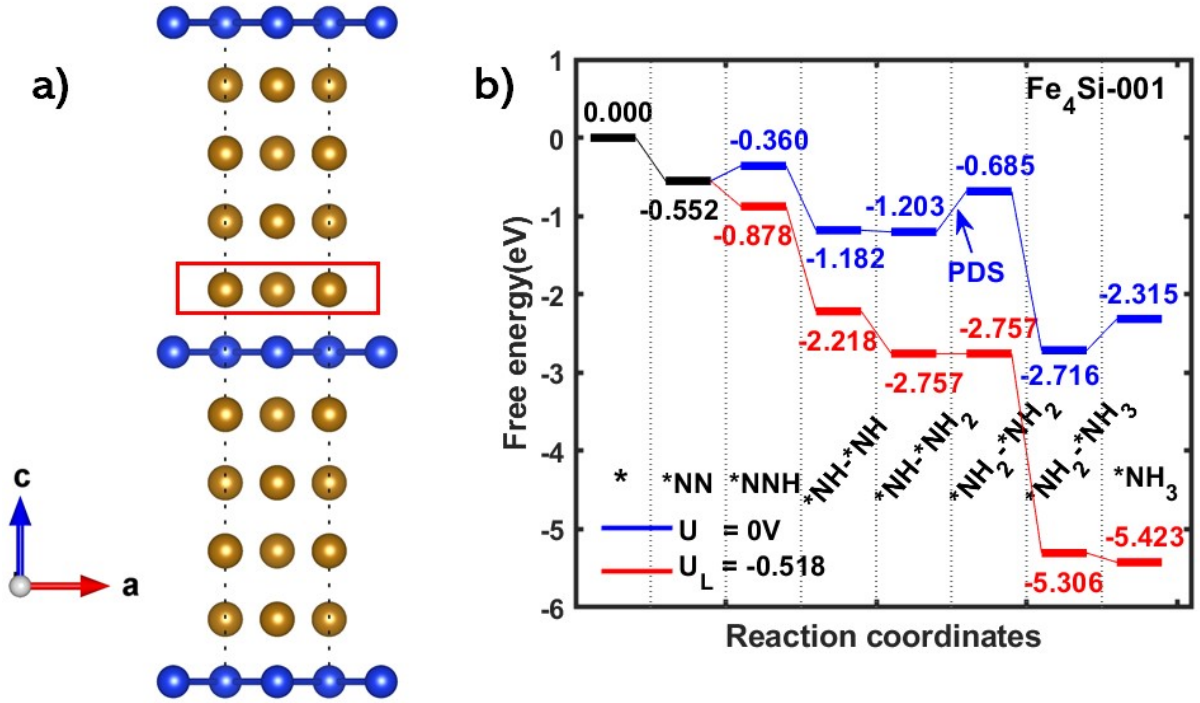

Figure S2: a): Structure of Fe_4Si conventional cell and the specific surface termination we used in our calculation. The motivation for picking this layer is a previous work reporting subsurface Si-doping on iron. b): Free energy diagram of $Fe_4Si(100)$ with the largest free energy change as 0.518 eV. Color map: bronze—Fe; blue—Si.

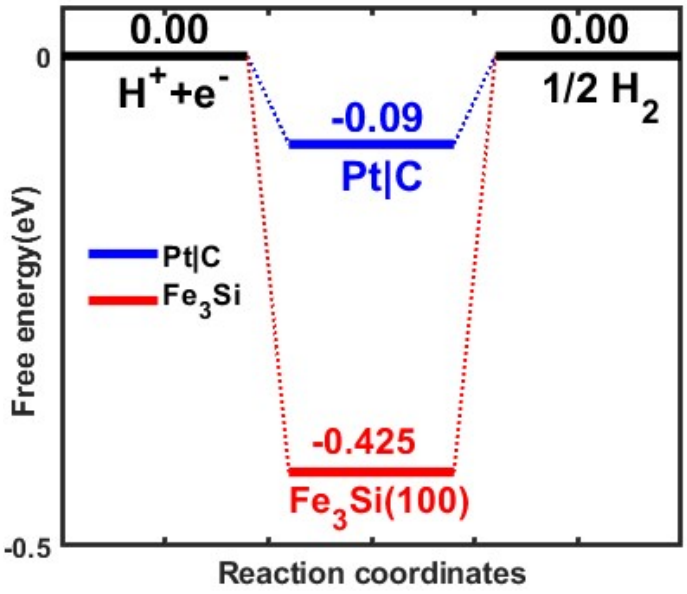

Figure S3: Proton adsorption free energy on $Fe_3Si(100)$ deviates a lot from the optimal value, indicating a bad HER performance.

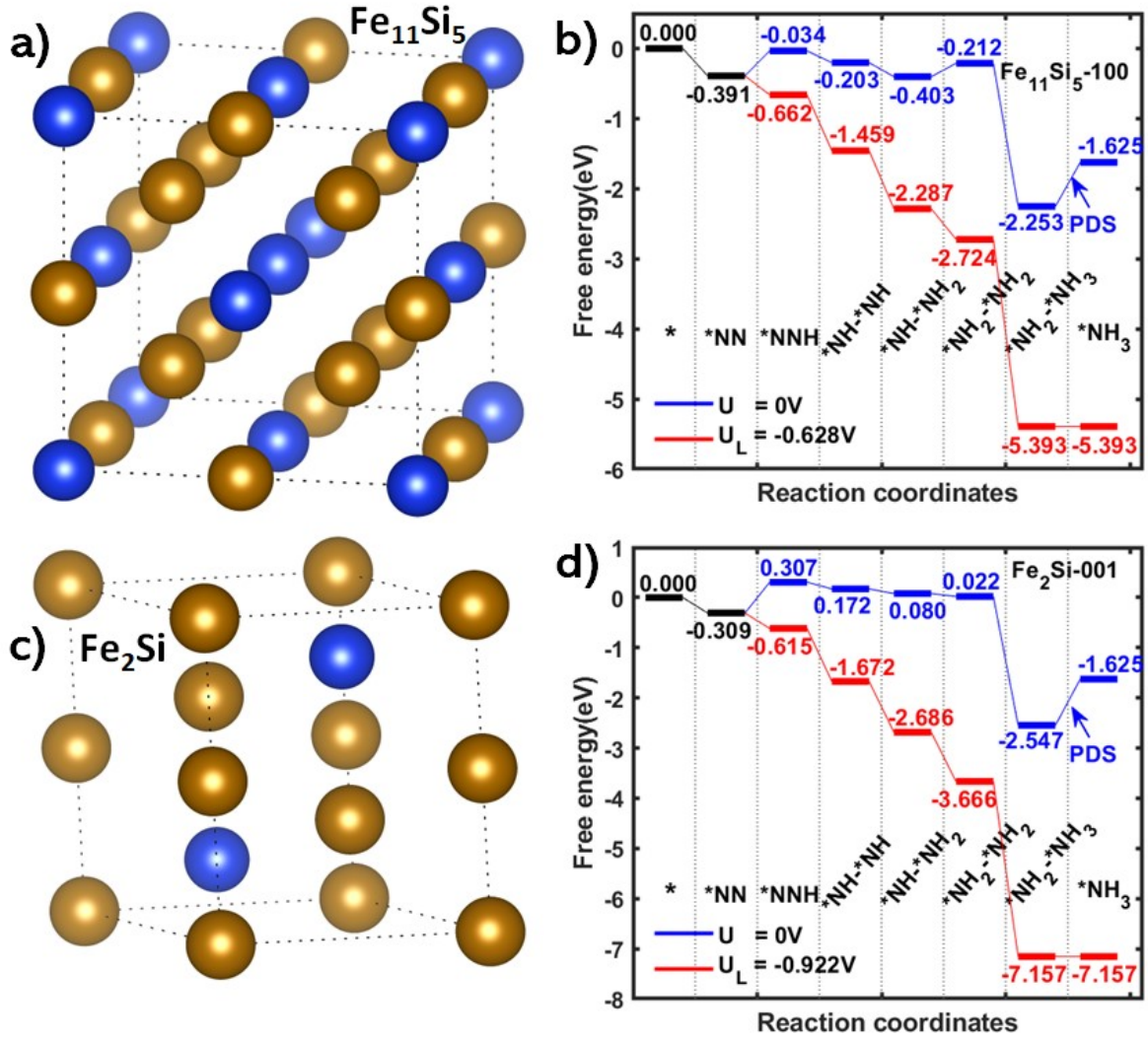

Figure S4: a)&c): Structures of $Fe_{11}Si_5$ and Fe_2Si conventional cell. The specific lattice parameters can be found in manuscript. b)&d): Free energy diagrams of $Fe_{11}Si_5$(100) and Fe_2Si(001). Color map: bronze—Fe; blue—Si.

Fe_4Si	(100)	(010)
Endon	**$E_{ad} > 0$**	**$E_{ad} > 0$**
Horizontal	**To Endon**	**To Endon**
Sideon	**No adsorption**	**No adsorption**

Table S1: N_2 adsorption on different surfaces of {100} family of Fe_4Si, where only (001) surface enables stable adsorption for dinitrogen molecule.

	*NN	*NNH	*NHNH	$*NHNH_2$	$*NH_2NH_2$	$*NH_2$	$*NH_3$
400 eV	-1017.734495	-1020.744881	-1024.260399	-1027.952395	-1031.019724	-1036.547584	-1020.599193
500 eV	-1017.731394	-1020.741959	-1024.256706	-1027.940628	-1031.000059	-1036.527445	-1020.583509

Table S2: Comparison of total free energies of all e-N2RR intermediates on Fe_3Si with energy cutoff as 400 eV and 500 eV, separately. The $Fe_3Si(100)$ slab model has 96 Fe atoms and 32 Si atoms.

FeSi	ΔG of 1st hydrogenation step on (100)
Endon	**0.868 eV**
Horizontal	**N/A**
Sideon	**0.974 eV**

Table S3: Activity of e-N2RR on FeSi(100) surface. The free energies of 1st hydrogenation step for all adsorption modes are even worse than pristine iron.