Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary Information

Synergetic Effect between Non-metals and Dual Metal Catalysts for Nitrogen Reduction Reaction

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Table S1. Calculated ΔZPE and TΔS of gas molecules and intermediates on catalyst, the * represent end-on mode, while ** represent side-on mode.

Fe_2@BN_4			**Fe_2@SN_4**		
species	ΔZPE	TΔS	species	ΔZPE	TΔS
N-N**	0.20	0.11	N-N**	0.18	0.07
N-NH**	0.50	0.12	N-NH**	0.50	0.10
NH-NH**	0.81	0.13	NH-NH**	0.82	0.12
NH-NH2**	1.16	0.14	NH-NH2**	1.17	0.13
NH2-NH2**	1.34	0.20	NH2-NH2**	1.35	0.19
NH2**	0.70	0.07	NH2**	0.67	0.11
NH3**	1.02	0.16	NH3**	1.02	0.18
Co_2@BN4			Co_2@PN4		
species	ΔZPE	TΔS	species	ΔZPE	TΔS
N-N**	0.20	0.11	N-N*	0.21	0.14
N-NH**	0.50	0.11	NNH*	0.48	0.15
NH-NH**	0.82	0.10	NNH2*	0.81	0.15
NH-NH2**	1.19	0.11	N*	0.09	0.03
NH2-NH2**	1.49	0.16	NH*	0.38	0.05
NH2**	0.73	0.07	NH2*	0.72	0.06
NH3**	1.02	0.15	NH3*	1.03	0.13
Ni_2@PN4			gas		
species	ΔZPE	TΔS	species	ΔZPE	TΔS
N-N**	0.19	0.13	NH3	0.92	0.59
N-NH**	0.51	0.10	H2	0.27	0.40
NH-NH**	0.81	0.12	N2	0.15	0.59
NH-NH2**	1.17	0.12			
NH2-NH2**	1.30	0.17			
NH2**	0.71	0.06			
NH3**	1.02	0.14			

Table S2. The free energy of 15 catalysts via distal, alternating and enzymetic processes.

	Distal process						
Surface	N2	NNH	NNH2	N	NH	NH2	NH3
Fe2@NN4	-0.84	0.15	0.24	-0.50	-0.82	-1.35	-1.63
Fe2@BN4	-0.81	-0.48	-0.34	-1.03	-1.54	-2.42	-1.46
Fe2@ON4	-1.02	-0.15	-0.55	-0.79	-1.58	-2.26	-1.65
Fe2@SN4	-1.13	-0.84	-1.00	-1.69	-2.07	-2.71	-2.36
Fe2@PN4	-0.72	-0.11	-0.41	-0.81	-1.48	-2.43	-1.46
Co2@NN4	-0.84	0.23	0.25	-0.13	-0.13	-1.86	-1.51
Co2@BN4	-0.73	-0.35	-0.26	-0.94	-1.31	-1.91	-1.52
Co2@ON4	-1.13	-0.11	-0.24	-0.43	-1.25	-1.79	-1.69
Co2@SN4	-0.68	-0.13	0.16	-0.58	-1.01	-1.32	-1.21
Co2@PN4	-0.37	-0.03	-0.09	-0.47	-1.15	-1.40	-1.17
Ni2@NN4	-0.79	0.45	0.88	0.98	0.05	-1.02	-1.54
Ni2@BN4	-0.54	0.39	0.35	0.29	-0.41	-1.44	-1.53
Ni2@ON4	-0.58	-0.28	-0.30	0.36	-0.87	-1.77	-1.71
Ni2@SN4	-0.17	0.74	0.40	0.74	-0.13	-1.06	-0.78
Ni2@PN4	-0.36	0.69	0.66	0.92	-0.21	-1.39	-1.11
	Alternating process						
Surface	N2	NNH	NHNH	NHNH2	NH2NH2	NH2	NH3
Fe2@NN4	-0.87	0.15	0.63	-0.38	-0.56	-1.29	-1.68
Fe2@BN4	-0.81	-0.48	0.12	-0.31	0.30	-0.87	-1.51
Fe2@ON4	-1.02	-0.15	-0.33	0.28	0.50	-2.25	-1.65
Fe2@SN4	-1.13	-0.84	-0.03	-0.82	-0.41	-2.30	-2.36
Fe2@PN4	-0.72	-0.11	0.04	-0.34	0.52	-1.98	-1.46
Co2@NN4	-0.85	0.21	0.68	-0.32	-0.35	-1.87	-1.51
Co2@BN4	-0.73	-0.35	0.40	-0.03	0.69	-0.91	-1.52
Co2@ON4	-1.13	-0.11	-0.16	0.11	0.27	-1.76	-1.69
Co2@SN4	-0.68	-0.14	0.18	0.37	0.39	-1.55	-1.21
Co2@PN4	-0.37	-0.03	0.27	0.14	-0.39	-1.66	-1.17
Ni2@NN4	-0.82	0.42	0.60	-0.05	0.39	-0.98	-1.57
Ni2@BN4	-0.54	0.39	0.52	0.35	0.29	-0.76	-1.53
Ni2@ON4	-0.58	-0.28	-0.26	0.20	0.31	-1.64	-1.71
Ni2@SN4	-0.17	0.74	0.69	0.52	0.45	-1.10	-0.78
Ni2@PN4	-0.36	0.69	0.99	0.43	0.48	-0.53	-1.11
	Ensymatic process						
Surface	N2	NNH	NHNH	NHNH2	NH2NH2	NH2	NH3

Fe2@NN4	0.05	0.23	0.28	-0.16	0.36	-1.53	-1.57
Fe2@BN4	0.07	0.18	-0.08	-0.19	-1.14	-0.87	-1.56
Fe2@ON4	-0.37	-0.15	-0.55	-0.53	-1.22	-2.25	-1.69
Fe2@SN4	-0.82	-0.62	-1.06	-1.15	-2.13	-2.37	-2.41
Fe2@PN4	-0.07	0.13	-0.24	0.08	-1.18	-2.33	-1.36
Co2@NN4	-0.12	0.49	0.49	-0.05	0.09	-1.47	-1.67
Co2@BN4	-0.25	0.11	0.10	0.19	0.45	-0.89	-1.38
Co2@ON4	-0.47	0.10	-0.38	-0.32	-0.98	-1.80	-1.79
Co2@SN4	-0.29	0.07	0.06	0.20	-0.57	-1.50	-1.50
Co2@PN4	-0.19	0.20	-0.03	-0.11	-0.68	-1.66	-1.21
Ni2@NN4	-0.55	0.74	0.36	-0.04	0.04	-1.45	-1.93
Ni2@BN4	0.02	0.44	0.53	0.22	0.75	-0.76	-1.62
Ni2@ON4	-0.53	-0.14	-0.25	-0.13	-0.38	-1.73	-1.73
Ni2@SN4	-0.66	0.55	0.55	0.51	0.27	-1.18	-1.41
Ni2@PN4	0.13	0.46	0.61	0.24	0.55	-1.31	-0.98

Table S3. The bader charge Q_{N2} and bond length d_{N-N} of N_2 adsorbed on 15 catalysts with end-on and side-on configurations; the binding energy E_b of transition metal atom pairs anchored on the slab calculated by the energies of metal atoms in the vacuum and the bulk metal (E_{coh}).

Surface	$Q_{N2\text{-end-on}}$	$d_{N\text{-}N\text{-end-on}}$	$Q_{N2\text{-side -on}}$	$d_{N\text{-}N\text{-side-on}}$	E_b(vacuum)	E_b(bulk)	E_{coh}
Fe2@NN4	0.33	1.17	0.57	1.20	5.11	4.02	4.28
Fe2@BN4	0.51	1.17	0.71	1.21	5.46	4.36	4.28
Fe2@ON4	0.51	1.16	0.70	1.22	4.36	3.25	4.28
Fe2@SN4	0.58	1.17	0.67	1.22	3.03	1.94	4.28
Fe2@PN4	0.56	1.17	0.79	1.23	4.90	3.81	4.28
Co2@NN4	0.35	1.16	0.47	1.18	5.39	2.72	4.39
Co2@BN4	0.44	1.16	0.57	1.20	5.76	3.09	4.39
Co2@ON4	0.49	1.16	0.52	1.19	4.65	1.98	4.39
Co2@SN4	0.53	1.16	0.63	1.19	4.80	2.13	4.39
Co2@PN4	0.51	1.16	0.63	1.19	5.36	2.69	4.39
Ni2@NN4	0.23	1.16	0.42	1.14	5.45	1.33	4.44
Ni2@BN4	0.35	1.16	0.49	1.18	5.33	1.21	4.44
Ni2@ON4	0.46	1.16	0.47	1.18	4.79	0.67	4.44
Ni2@SN4	0.40	1.16	0.32	1.14	5.04	0.92	4.44
Ni2@PN4	0.41	1.16	0.48	1.19	5.51	1.39	4.44
Fe@SN4	0.32	1.14	0.33	1.17	5.39	4.31	4.28

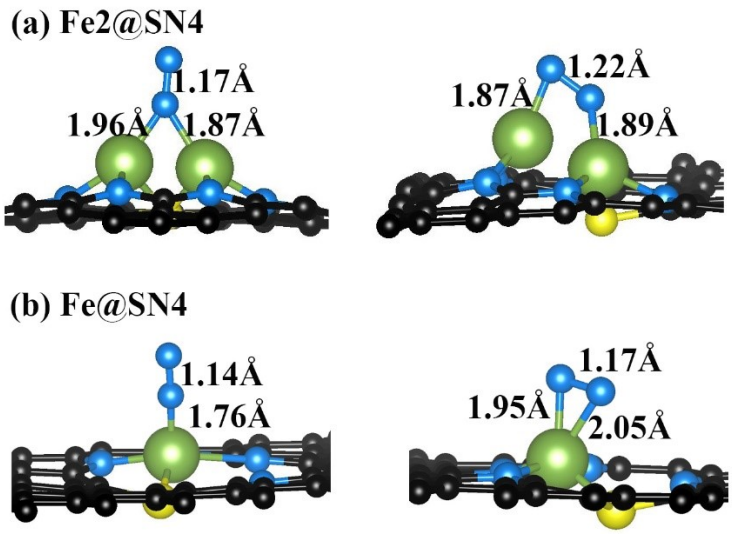

Figure S1. The structures of N_2 adsorbed on (a) $Fe_2@SN_4$ and (b) $Fe_2@SN_4$ with end-on and side-on configurations.

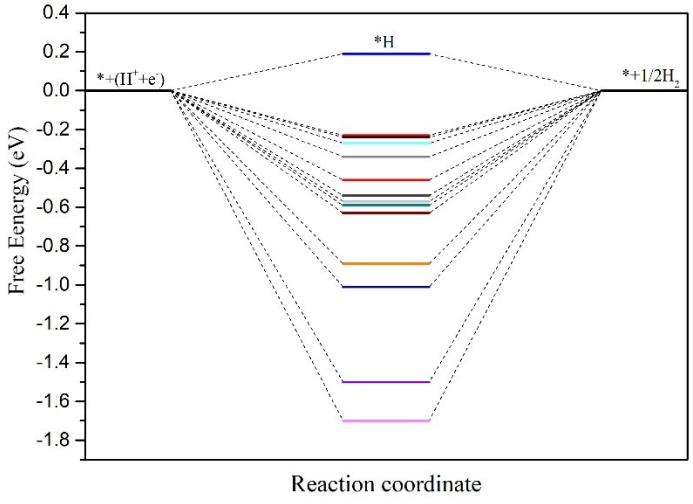

Figure S2. Free energy diagram of DACs for HER.

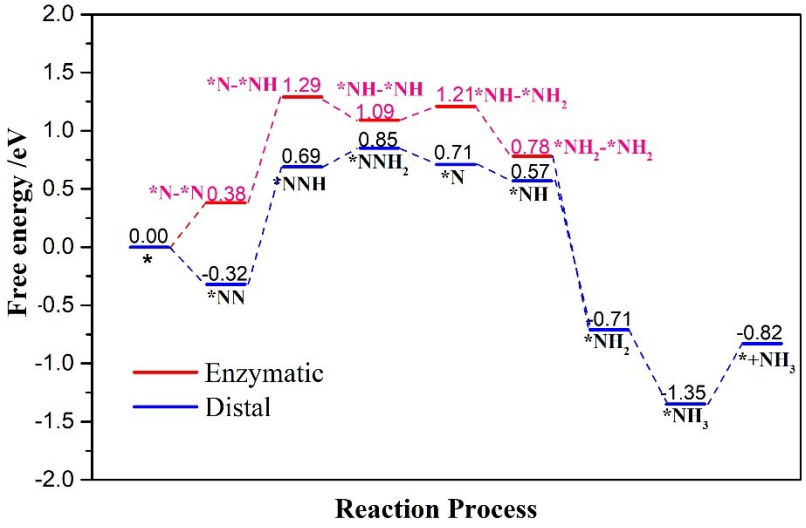

Figure S3. The calculated free energy profiles for NRR through enzymatic mechanism and distal mechanism on Fe@SN_4.