Supporting Information

Design of a High-Performance Electrocatalyst for N_2 Conversion to NH_3 by Trapping Single Metal Atoms on Stepped CeO_2

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Table S1. The binding energy (E_b) of 28 M anchored on CeO_2-S with different cutoff energy.

Energy cutoff / eV	E_b / eV			
	Sc	Ti	V	Cr
400	-8.90	-9.48	-5.87	-4.84
450	-8.89	-9.43	-5.86	-4.84
	Mn	Fe	Co	Ni
400	-4.72	-5.58	-5.41	-4.51
450	-4.64	-5.58	-5.53	-4.58
	Cu	Zn	Y	Zr
400	-3.96	-2.18	-8.72	-10.95
450	-3.95	-2.20	-8.73	-10.93
	Nb	Mo	Ru	Rh
400	-7.33	-5.49	-5.37	-4.82
450	-7.34	-5.48	-5.28	-4.89
	Pd	Ag	Cd	Hf
400	-3.70	-2.69	-1.00	-8.31
450	-3.69	-2.67	-0.98	-8.40
	Ta	W	Re	Os
400	-11.49	-6.64	-5.60	-6.26
450	-11.59	-6.59	-5.56	-6.26
	Ir	Pt	Au	Hg
400	-6.23	-5.41	-3.20	0.13
450	-6.27	-5.40	-3.20	0.06

Table S2. The binding energy (E_b) of Mo anchored on CeO_2-S and the adsorption energy (E_{ads}) of *N_2 with end-on configuration on Mo/CeO_2-S with different parameters such as lattice constant of the cell, *k*-point grids, and the criterion of force convergence.

Mo/CeO_2-S	Lattice constant	*k*-point grids	Force convergence criterion
	***a*=7.65 Å, *b*=13.25 Å**	**2×2×1**	**0.05 eV/Å**
E_b / eV	-5.49	-5.49	-5.49
E_{ads} / eV	-1.09	-1.09	-1.09
	***a*=15.30 Å, *b*=13.25 Å**	**4×2×1**	**0.02 eV/Å**
E_b / eV	-5.45	-5.47	-5.47
E_{ads} / eV	-1.16	-1.07	-1.11

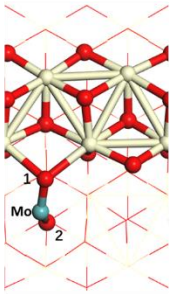
Table S3. Calculated vibrational frequencies, zero point energies and entropy of different adsorption species of Mo/CeO_2-S and Ru/CeO_2-S through distal, alternating and enzymatic mechanism, where the * denotes the adsorption site, therefore *N≡N and *N≡*N represent the end-on and side-on configurations respectively.

	Mechanism	Adsorption Species	Vibrational Frequencies/cm^{-1}	E_{zpe} / eV	TS / eV
Mo/CeO_2-S	Distal	*N≡N	2135.09 388.40 346.17 265.56 51.93 22.67	0.20	0.19
		*N=NH	3132.35 1574.01 1227.99 521.18 518.47 382.57 256.80 75.37 42.99	0.48	0.17
		*N-NH_2	3481.24 3374.49 1594.47 1438.44 1200.71 538.43 409.39 366.05 243.60 171.08 57.76	0.80	0.15
		*N	942.35 365.99 254.79	0.10	0.04
		*NH	3426.20 893.90 708.57 367.89 194.09 124.40	0.35	0.09
		*NH_2	3501.99 3212.30 1491.03 782.47 615.82 571.84 329.14 127.15	0.66	0.07
		*NH_3	3410.06 2653.00 2591.39 1586.09 1492.12 1345.89 877.01 766.74 495.87 449.79 220.56 184.47	1.00	0.08
	Alternating	*NH=NH	3302.86 3193.08 1495.08 1360.06 1266.13 903.01 551.26 449.42 282.26 213.71 71.97 35.24	0.81	0.19
		*NH-NH_2	3536.94 3408.06 2633.20 1603.15 1552.88 1254.20 1220.79 911.44 602.90 512.53 341.93 285.32 216.38 79.00	1.13	0.13
		*NH_2-NH_2	3380.01 3244.76 3061.59 3027.33 1685.65 1610.13 1466.03 1382.18 1149.51 1113.45 874.53 628.85 483.34 440.68 208.32 174.96 126.37	1.49	0.13

	Enzymatic	*N≡*N	1753.42 582.80 402.00 118.77 87.84	0.18	0.11
		*N=*NH	3343.22 1127.35 1048.79 637.10 516.76 431.88 230.84 108.24 62.22	0.47	0.15
		*NH=*NH	3336.08 3293.20 1317.89 1127.21 1011.62 733.44 722.01 549.60 501.61 248.81 110.88 49.23	0.81	0.15
		NH-NH_2	3460.25 3357.04 2649.31 1639.29 1378.56 1173.63 1137.06 1071.02 796.20 688.75 419.11 264.98 203.22 96.91	1.14	0.11
		NH_2-NH_2	3529.25 3387.01 3376.03 2821.67 1494.82 1480.25 856.19 795.23 642.77 627.39 599.71 491.71 428.07 321.77 197.15 165.07 119.51 106.44	1.33	0.20
		NH_2-NH_3	3482.34 3389.09 3362.90 2646.15 2590.92 1594.20 1540.11 1518.68 1376.30 881.88 811.94 713.59 593.70 507.17 447.97 421.57 382.54 237.53 190.08 133.99 75.63	1.67	0.20
Ru/CeO_2-S	Distal	*N≡N	2113.37 435.66 395.14 366.32 74.52 41.45	0.21	0.16
		*N=NH	3188.90 1703.16 1162.44 552.74 511.31 391.47 269.26 69.54 50.03	0.49	0.17
		*N-NH_2	3433.05 2391.12 1518.51 1476.65 1198.72 915.24 672.18 394.59 337.56 170.81 158.86	0.79	0.1
		*N	1052.66 190.13 133.50	0.09	0.08
		*NH	3394.80 954.41 709.47 442.31 148.51	0.35	0.05
		*NH_2	3478.51 3389.71 1473.61 815.19 714.52 555.95 460.94 148.66 27.84	0.69	0.14
		*NH_3	3467.06 3399.98 3243.04 1603.87 1581.07 1228.92	1.03	0.14

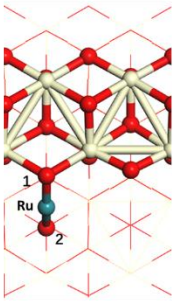
			714.83	644.12	395.12		
			163.00	144.64	86.87		
	Alternating	*NH=NH	3273.53	3109.68	1501.56	0.82	0.13
			1430.90	1278.42	1163.88		
			503.55	467.54	275.67		
			132.89	75.96			
		*NH-NH_2	3412.35	3342.76	3193.92	1.14	0.12
			1598.29	1403.98	1212.76		
			1114.81	886.01	627.54		
			597.14	338.85	294.11		
			208.20	94.60			
		*NH_2-NH_2	3422.71	3343.17	3113.53	1.49	0.24
			2847.58	1636.23	1594.61		
			1416.26	1287.78	1174.11		
			1091.44	881.43	704.78		
			486.72	423.31	255.93		
			183.06	162.56	4.39		
	Enzymatic	*N≡*N	1967.21	451.77	202.24	0.18	0.11
			143.61	131.19			
		*N=*NH	3132.08	1447.12	994.69	0.45	0.11
			702.89	466.18	272.12		
			156.65	135.05			
		*NH=*NH	3243.39	3061.03	1412.58	0.83	0.12
			1259.99	1127.61	997.93		
			785.68	509.45	404.08		
			274.85	168.65	113.60		
		NH-NH_2	3341.08	3140.31	2826.21	1.16	0.16
			1603.17	1371.57	1177.60		
			1105.08	1049.87	990.11		
			812.41	507.22	371.42		
			239.62	151.63	38.80		
		NH_2-NH_2	3480.03	3389.78	3364.55	1.36	0.20
			3308.80	1548.67	1457.24		
			803.66	753.89	722.65		
			607.98	564.96	540.40		
			514.97	254.58	245.12		
			186.80	103.42	91.35		
		NH_2-NH_3	3434.97	3378.44	3322.53	1.71	0.21
			3120.18	3060.40	1608.81		
			1589.20	1453.46	1374.49		
			871.51	863.02	758.34		
			683.40	537.53	393.41		
			310.27	251.28	229.83		
			183.57	132.92	100.52		

(a)



	Mo-O1 / Å	Mo-O2 / Å
*	1.795	1.840
*N≡N	1.784	1.822
*N=NH	1.854	1.904
*N-NH_2	1.829	1.867
*N	1.835	1.883
*NH	1.837	1.878
*NH_2	1.786	1.798
*NH_3	1.796	1.820

(b)



	Ru-O1 / Å	Ru-O2 / Å
*	1.915	1.949
*N≡N	1.896	1.982
*N=NH	1.861	1.893
*N-NH_2	1.858	1.913
*N	1.913	1.987
*NH	1.812	1.922
*NH_2	1.820	1.865
*NH_3	1.867	1.920

Figure S1. The change of lengths of (a) Mo-O and (b) Ru-O bonds in NRR process through distal mechanism, in which the * denotes the adsorption site.

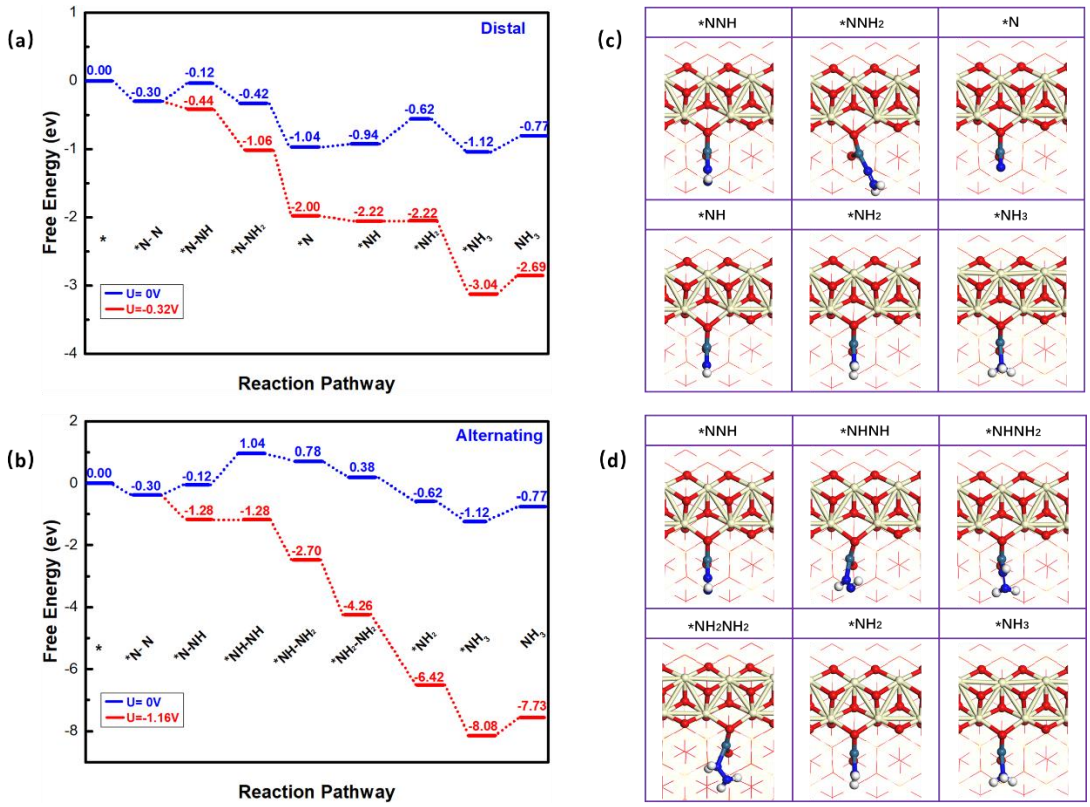


Figure S2. Free energy diagram for NRR on Os/CeO_2-S following (a) distal and (b) alternating pathway. The corresponding configurations of NRR intermediates are shown in the (c) and (d) respectively. Color scheme: N, navy blue; H, white; Ce, yellow; O, red; and Os, blue-green.

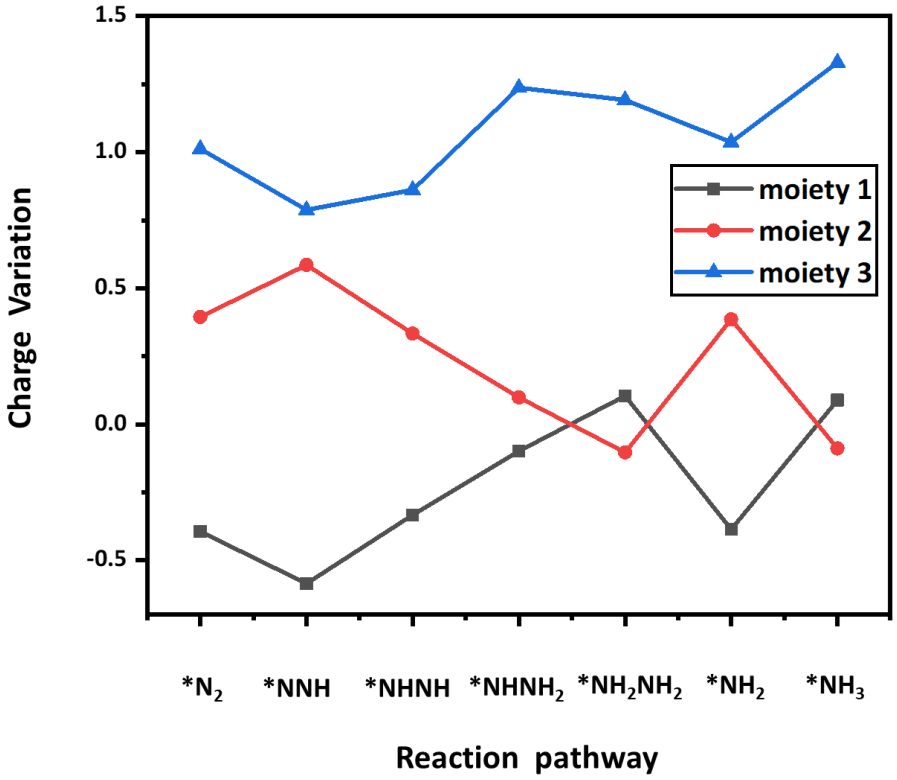


Figure S3. Charge variation for each moiety along the alternating pathway on Mo/CeO_2-S. Moieties 1, 2 and 3 represent the M/CeO_2-S, the adsorbed N_xH_y species, and the CeO_2-S substrate, respectively.