Electronic Supplementary Information

Anchored Atomic Tungsten on B_{40} Cage: a Highly Active and Selective Single-Atom Catalyst for Nitrogen Reduction

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Table S1. Calculated relative energies of $B_{40}M$ in different spin states at the (U)PBE0-D3/LanL2DZ~6-31G(d) level.

M of $B_{40}M$	Relative energy/eV ($<S^2>$)				
	singlet	doublet	triplet	quartet	quintet
Sc (hep[a])		**0.00 (0.77)**		0.64 (3.78)	
Sc (hex[a])		0.60 (0.77)		1.28 (3.78)	
Ti (hep)	0.12		**0.00 (2.04)**		0.81 (6.06)
Ti (hex)	0.62		0.84 (2.10)		1.68 (6.06)
V (hep)		0.55 (0.86)		**0.00 (3.82)**	
V (hex)		1.17 (1.62)		0.73 (4.19)	
Cr (hep)	1.86		0.95 (3.01)		**0.00 (6.25)**
Cr (hex)	2.52		1.64 (2.74)		0.58 (6.68)
Mn (hep)		1.33 (0.82)		**0.00 (4.14)**	
Mn (hex)		2.14 (0.97)		0.64 (4.59)	
Fe (hep)	0.88		**0.00 (2.74)**		0.30 (6.09)
Fe (hex)	1.88		0.47 (2.35)		0.65 (6.06)
Co (hep)		**0.00 (0.80)**		1.27 (3.80)	
Co (hex)		0.88 (0.84)		1.17 (3.79)	
Ni (hep)	**0.00**		1.39 (2.03)		3.24 (6.07)
Ni (hex)	0.82		1.79 (2.02)		3.70 (6.06)
Cu (hep)		**0.00 (0.76)**		1.91/3.80	
Cu (hex)		0.34 (0.76)		2.26/3.80	
Mo (hep)	**0.00**		0.01 (2.09)		0.06 (6.07)
Mo (hex)	0.43		0.61 (2.08)		1.03 (6.08)
W (hep)	0.09	□	**0.00 (2.03)**	□	0.08 (6.06)
W (hex)	0.68		0.91 (2.09)		1.29 (6.06)
Pd (hep)	**0.00**		1.66 (2.03)		3.42 (6.05)
Pd (hex)	0.58		1.93 (2.01)		3.82 (6.04)
Pt (hep)	**0.00**		1.51 (2.03)		3.22 (6.05)
Pt (hex)	0.76		2.04 (2.02)		3.79 (6.04)
Ru (hep)	0.07		**0.00 (2.04)**		1.21 (6.05)
Ru (hex)	0.57		0.41 (2.03)		2.07 (6.05)
Rh (hep)		**0.00 (0.77)**		1.48 (3.78)	
Rh (hex)		0.54 (0.76)	□	1.79 (3.78)	□

a: M(hep)/(hex) indicates the metal M resides in the center of a heptagonal/hexagonal ring of B_{40}.

Table S2. Calculated electronic energies of metal (E(M)), B_{40} (E(B_{40})), metalloborospherene (E(B_{40}M)), and the corresponding binding energies (E_b) of different atomic metals on B_{40} at the (U)PBE0-D3/LanL2DZ~6-31G(d) level.

M	E(M) (a.u.)	E(B_{40}) (a.u.)	E(B_{40}M) (a.u.)	E_b (eV)
Sc	-46.3264	-992.5674	-1039.0432	4.07
Ti	-57.8614	-992.5674	-1050.6455	5.90
V	-71.1709	-992.5674	-1063.8788	3.82
Cr	-86.1972	-992.5674	-1078.8674	2.80
Mn	-103.6889	-992.5674	-1096.4699	5.81
Fe	-123.3017	-992.5674	-1115.9756	2.90
Co	-144.9499	-992.5674	-1137.6349	3.20
Ni	-169.1733	-992.5674	-1161.8812	3.82
Cu	-196.0389	-992.5674	-1188.6728	1.81
Mo	-67.3620	-992.5674	-1060.0873	4.30
W	-67.5996	-992.5674	-1060.3513	5.01
Pd	-126.6666	-992.5674	-1119.3437	2.99
Pt	-119.0371	-992.5674	-1111.7675	4.43
Ru	-93.7601	-992.5674	-1086.4787	4.12
Rh	-109.4003	-992.5674	-1102.1187	4.11

Table S3. Calculated NPA charge of $B_{40}W$ and N_2 fragments of $B_{40}W$-N_2 at the at the (U)PBE0-D3/LanL2DZ~6-311G(d,p)//(U)PBE0-D3/LanL2DZ~6-31G(d) level.

	NPA charge (e)	
	$B_{40}W$	N_2
$B_{40}W$-$N_{2side-on}$	0.25	-0.14
$B_{40}W$-$N_{2end-on}$	-0.04	0.04

Table S4. Calculated electronic energy (*E.E.*) at the (U)PBE0-D3/LanL2DZ~6-311G(d,p)//(U)PBE0-D3/LanL2DZ~6-31G(d) level, thermal correction (*T. C.*) at the (U)PBE0-D3/LanL2DZ~6-31G(d) level, and the corresponding Gibbs free energy (*G*) of the selected *N_2 and *NNH intermediates along the NRR process.

	*N_2			*NNH		
M	*E.E.* (a.u.)	*T.C.* (a.u.)	*G* (a.u.)	*E.E.* (a.u.)	*T.C.* (a.u.)	*G* (a.u.)
Sc_end[a]	-1148.6401	0.1349	-1148.5052	-1149.1905	0.1444	-1149.0461
Ti_side[a]	-1160.2497	0.1378	-1160.1119	-1160.8308	0.1485	-1160.6823
Ti_end	-1160.2580	0.1353	-1160.1227	-1160.8107	0.1460	-1160.6646
V_end	-1173.4888	0.1353	-1173.3535	-1174.0391	0.1496	-1173.8895
Cr_end	-1188.4671	0.1333	-1188.3338	-1189.0044	0.1437	-1188.8607
Mn_end	-1206.0717	0.1329	-1205.9388	-1206.6121	0.1452	-1206.4668
Fe_end	-1225.5870	0.1357	-1225.4513	-1226.1240	0.1462	-1225.9777
Co_end	-1247.2350	0.1370	-1247.0980	-1247.7543	0.1499	-1247.6044
Cu_end	-1298.2642	0.1308	-1298.1335	-1298.7815	0.1449	-1298.6366
Mo_side	-1169.6856	0.1376	-1169.5480	-1170.2591	0.1460	-1170.1130
Mo_end	-1169.7065	0.1369	-1169.5696	-1170.2631	0.1470	-1170.1160
W_side	-1169.9615	0.1354	-1169.8260	-1170.5492	0.1460	-1170.4032
W_end	-1169.9810	0.1354	-1169.8456	-1170.5464	0.1449	-1170.4015
Ru_end	-1196.0614	0.1350	-1195.9264	-1196.6192	0.1457	-1196.4735

a: end/side indicates the N_2 is adsorbed in the form of end-on/side-on configuration.

Table S5. Calculated electronic energy (*E.E.*) at the (U)PBE0-D3/LanL2DZ~6-311G(d,p)//(U)PBE0-D3/LanL2DZ~6-31G(d) level, thermal correction (*T. C.*) at the (U)PBE0-D3/LanL2DZ~6-31G(d) level, and the corresponding Gibbs free energy (*G*) of the selected *NH_2 and *NH_3 intermediates along the NRR process.

	*NH_2			*NH_3		
M	*E.E.* (a.u.)	*T.C.* (a.u.)	*G* (a.u.)	*E.E.* (a.u.)	*T.C.* (a.u.)	*G* (a.u.)
Ti	-1106.7695	0.1538	-1106.6157	-1107.3615	0.1639	-1107.1976
Mo	-1116.1967	0.1536	-1116.0431	-1116.7960	0.1651	-1116.6309
W	-1116.4928	0.1520	-1116.3408	-1117.0694	0.1646	-1116.9048

Table S6. Calculated electronic energy (*E.E.*) at the (U)PBE0-D3/LanL2DZ~6-311G(d,p)//(U)PBE0-D3/LanL2DZ~6-31G(d) level, thermal correction (*T. C.*) at the (U)PBE0-D3/LanL2DZ~6-31G(d) level, and the corresponding Gibbs free energy (*G*) of the selected $B_{40}M$ and *H intermediates along the HER process.

	$B_{40}M$			*H		
M	*E.E.* (a.u.)	*T.C.* (a.u.)	*G* (a.u.)	*E.E.* (a.u.)	*T.C.* (a.u.)	*G* (a.u.)
Ti	-1050.7944	0.1313	-1050.6631	-1051.3881	0.1368	-1051.2512
Mo	-1060.2360	0.1312	-1060.1048	-1060.8240	0.1340	-1060.6900
W	-1060.4836	0.1274	-1060.3562	-1061.1132	0.1339	-1060.9793

Table S7. Calculated electronic energy (*E.E.*) at the (U)PBE0-D3/LanL2DZ~6-311G(d,p)//(U)PBE0-D3/LanL2DZ~6-31G(d) level, thermal correction (*T. C.*) at the (U)PBE0-D3/LanL2DZ~6-31G(d) level, and the corresponding Gibbs free energy (*G*) of all relevant structures along the NRR process.

Relevant structure along the NRR	*E.E.* (a.u.)	*T.C.* (a.u.)	*G* (a.u.)
N_2	-109.4289	-0.0128	-109.4417
H_2	-1.1682	-0.0014	-1.1695
NH_3	-56.5038	0.0159	-56.4880
$B_{40}W$	-1060.4836	0.1274	-1060.3562
$*N_{2side}$	-1169.9615	0.1354	-1169.8260
$*NNH_{side}$	-1170.5492	0.1460	-1170.4032
$*NHNH_{side}$	-1171.1613	0.1594	-1171.0019
$*NHNH_{2side}$	-1171.7866	0.1713	-1171.6153
$*N_2H_{4side}$	-1172.3476	0.1835	-1172.1641
*N	-1115.2490	0.1325	-1115.1165
*NH	-1115.8895	0.1437	-1115.7457
$*NH_2$	-1116.4928	0.1520	-1116.3408
$*NH_3$	-1117.0694	0.1646	-1116.9048
$*N_{2end}$	-1169.9810	0.1354	-1169.8456
$*NNH_{end}$	-1170.5464	0.1449	-1170.4015
$*NNH_2$	-1171.1772	0.1590	-1171.0182
$*NHNH_{end}$	-1171.1268	0.1577	-1170.9691
$*NHNH_{2end}$	-1171.7602	0.1690	-1171.5912

$*N_2H_{4end}$	-1172.3361	0.1808	-1172.1552