Enabling electrochemical reduction of nitrogen to ammonia at ambient conditions through rational catalyst design†

- Electronic Supplementary Information

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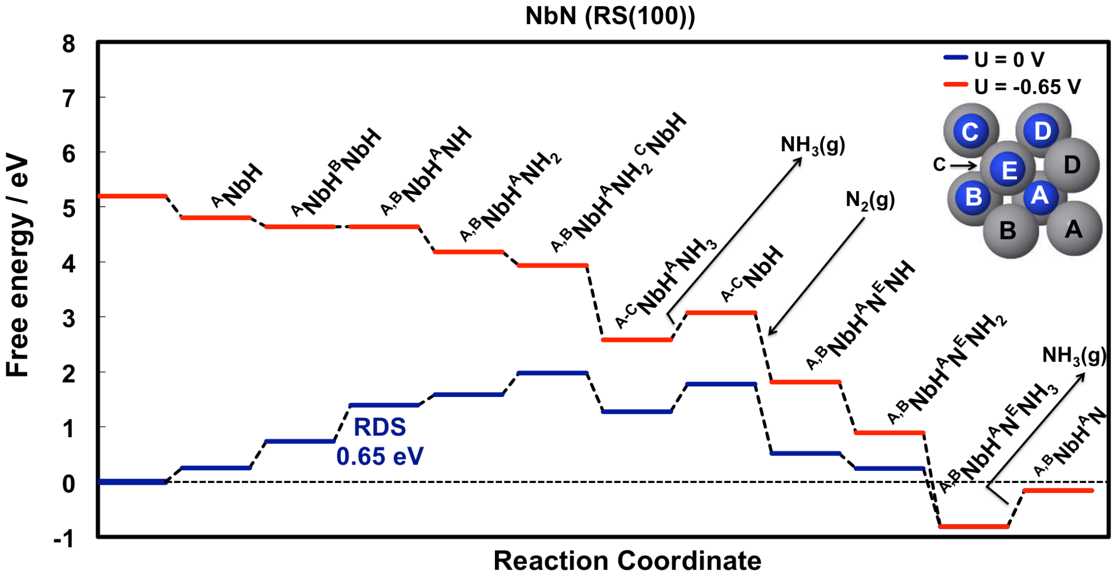
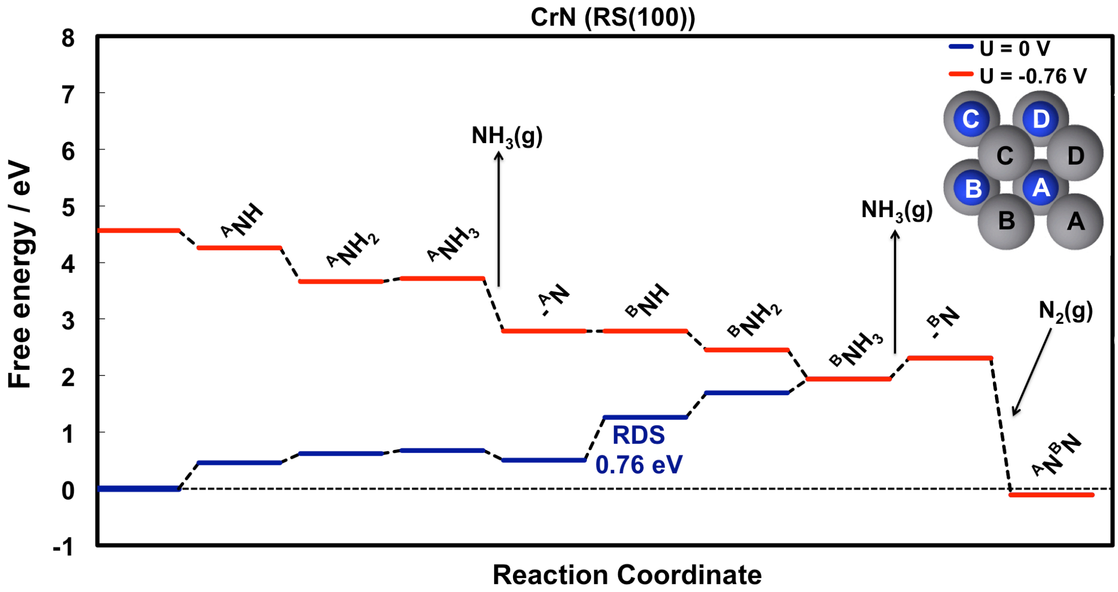
Table 1 Energy per metal-nitrogen pair (in eV) of the various metal nitride slabs. The energies are relative to the most stable facet for each nitride. Slabs that were found to be unstable upon relaxation are denoted with a hyphen.

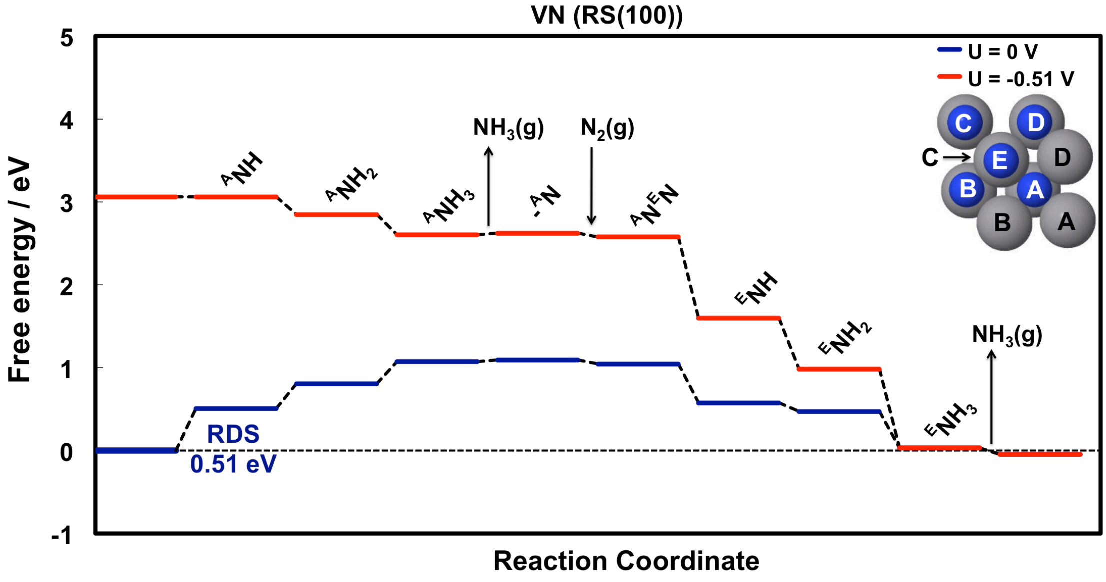
	Nitride	**RS(100)**	**RS(111)**	**ZB(100)**	**ZB(110)**
4th period	ScN	**0.00**	0.78	1.14	0.63
	TiN	**0.00**	0.32	0.94	0.84
	VN	**0.00**	0.26	0.67	0.57
	CrN	**0.00**	0.64	0.33	0.17
	MnN	**0.00**	0.06	0.08	0.03
	FeN	-	0.48	0.14	**0.00**
	CoN	-	0.25	0.16	**0.00**
	NiN	0.20	0.34	0.16	**0.00**
	CuN	**0.00**	0.21	0.18	0.08
5th period	YN	**0.00**	0.85	1.23	0.79
	ZrN	**0.00**	0.18	0.91	1.03
	NbN	**0.00**	0.13	0.87	0.84
	MoN	**0.00**	0.14	0.44	0.24
	RuN	-	-	0.05	**0.00**
	RhN	-	-	0.17	**0.00**
	PdN	-	-	0.06	**0.00**
	AgN	**0.00**	0.08	0.37	0.75
6th period	HfN	**0.00**	0.09	0.96	0.69
	TaN	**0.00**	0.01	0.66	0.65
	WN	-	-	-	-
	ReN	-	-	-	-
	OsN	-	-	0.05	**0.00**
	IrN	-	-	0.17	**0.00**
	PtN	-	-	-	-
	AuN	**0.00**	-	0.09	-

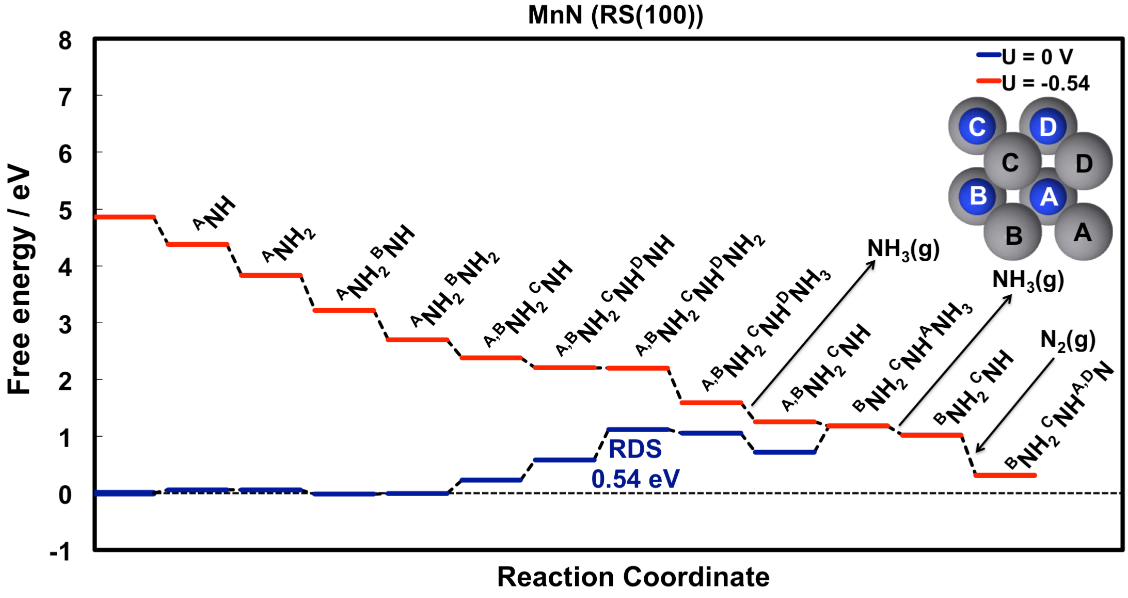
Free energy diagrams

The constructed free energy diagrams for the stable nitrides that exhibit reasonable catalytic activity towards electrochemical ammonia formation are illustrated in Fig. 1 for the (100) facet of RS structure as well as the (110) facet of ZB structure.






VN (RS(100))
Free energy / eV
5
4
3
2
1
0
-1
Reaction Coordinate
U = 0 V
U = -0.51 V
^{A}NH
$^{A}NH_2$
$^{A}NH_3$
$NH_3(g)$
^{A}N
$N_2(g)$
$^{A}N^{E}N$
^{E}NH
$^{E}NH_2$
$^{E}NH_3$
$NH_3(g)$
RDS
0.51 eV
C
D
C
E
D
B
A
B
A


MnN (RS(100))
Free energy / eV
8
7
6
5
4
3
2
1
0
-1
Reaction Coordinate
U = 0 V
U = -0.54
^{A}NH
$^{A}NH_2$
$^{A}NH_2{}^{B}NH$
$^{A}NH_2{}^{B}NH_2$
$^{A,B}NH_2{}^{C}NH$
$^{A,B}NH_2{}^{C}NH^{D}NH$
$^{A,B}NH_2{}^{C}NH^{D}NH_2$
$^{A,B}NH_2{}^{C}NH^{D}NH_3$
$NH_3(g)$
$^{A,B}NH_2{}^{C}NH$
$^{B}NH_2{}^{C}NH^{A}NH_3$
$NH_3(g)$
$^{B}NH_2{}^{C}NH$
$N_2(g)$
$^{B}NH_2{}^{C}NH^{A,D}N$
RDS
0.54 eV
C
D
C
D
B
A
B
A

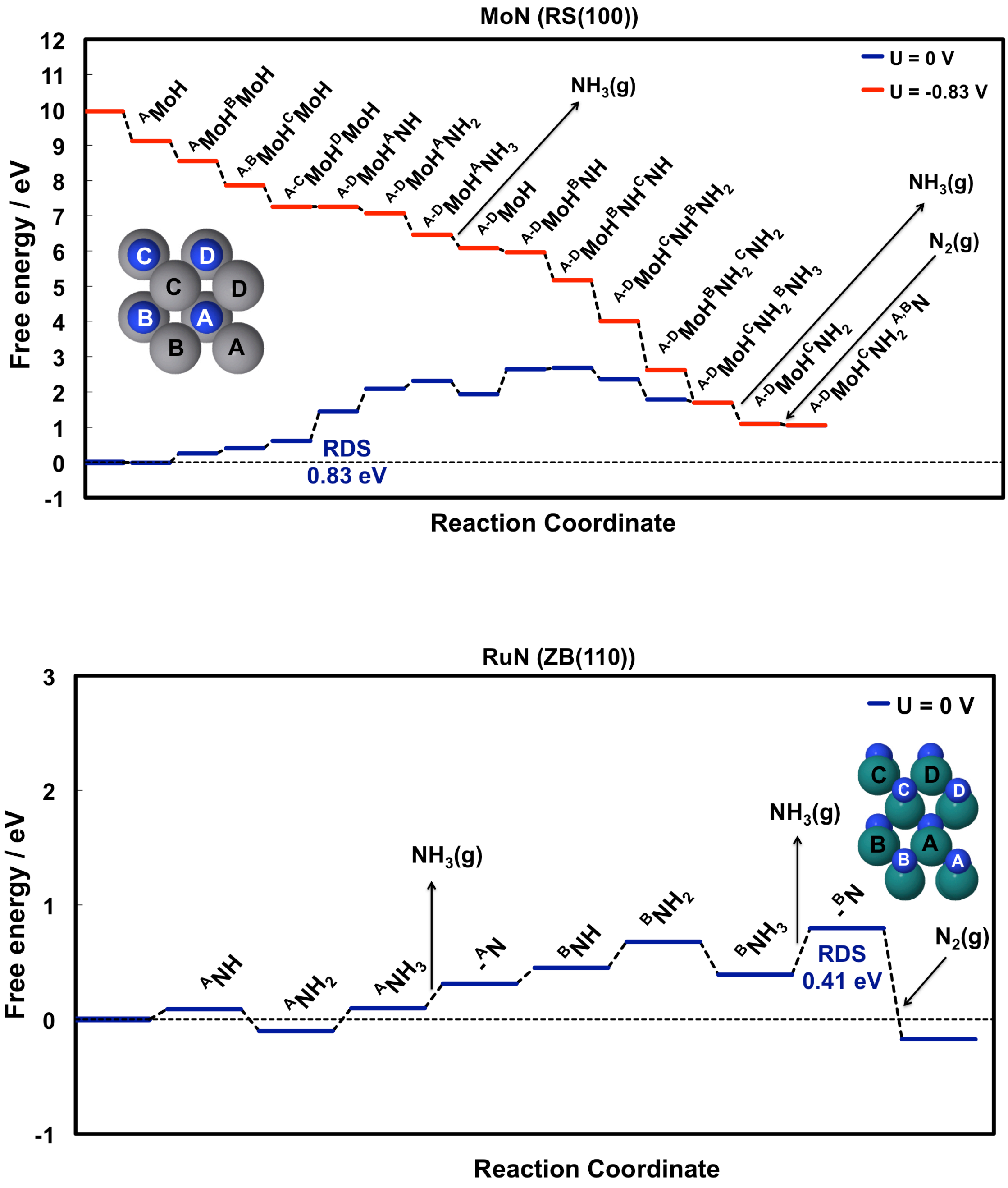


Fig. 1 Free energy diagram for NH_3 formation *via* an unconstrained Mars-van Krevelen mechanism on the (100) facet of RS and the (110) facet of ZB structures. The blue line shows the free energy of all the stable intermediates calculated at zero potential. The red line represents the free energy of all the stable intermediates at the onset potential.

To construct these free energy diagrams, the free energy of each elementary step is estimated at pH = 0 according to:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \qquad (1)$$

where ΔE is the reaction energy calculated using DFT. The zero-point energy correction (ΔE_{ZPE}) and entropy difference (ΔS) are calculated within a harmonic approximation (given in table 2 and 3 below). The effect of an applied bias, U, is included for all electrochemical reaction steps by shifting the free energy for reactions involving *n* electrons by $-neU$:[1]

$$\Delta G(U) = \Delta E + \Delta E_{ZPE} - T\Delta S - neU \qquad (2)$$

Table 2. Zero point energy and entropy contributions to the free energy of gas phase and adsorbed molecules at 300 K for RS nitrides (in eV).[a]

RS (100)	**TS**	**ZPE**
NH_3	0.74	0.89
H_2	0.41	0.27
N_2	0.6	0.15
$*N_2$	0.09	0.17
$*H_{on\ M}$	0.03	0.14
$*H_{on\ N}$	0.04	0.25
***2H**	0.07	0.69
***3H**	0.17	1.00
***N**	0.04	0.08
***NH**	0.06	0.34
$*NH_2$	0.07	0.69
$*NH_3$	0.18	0.99

[a]The values for gas phase molecules are taken from ref[2,3], and the values for adsorbed molecules are obtained from DFT calculations of vibrational normal modes.

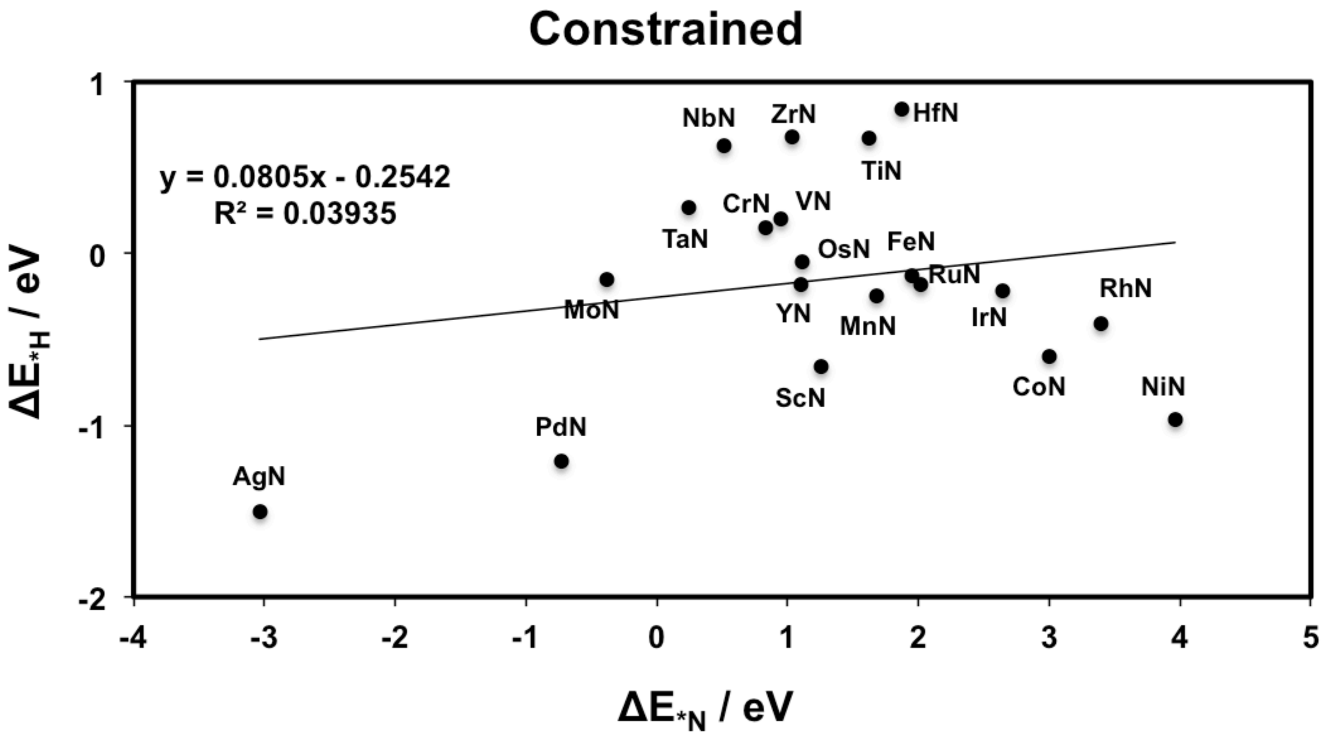
Table 3. Zero point energy and entropy contributions to the free energy of gas phase and adsorbed molecules at 300 K for ZB nitrides (in eV).[a]

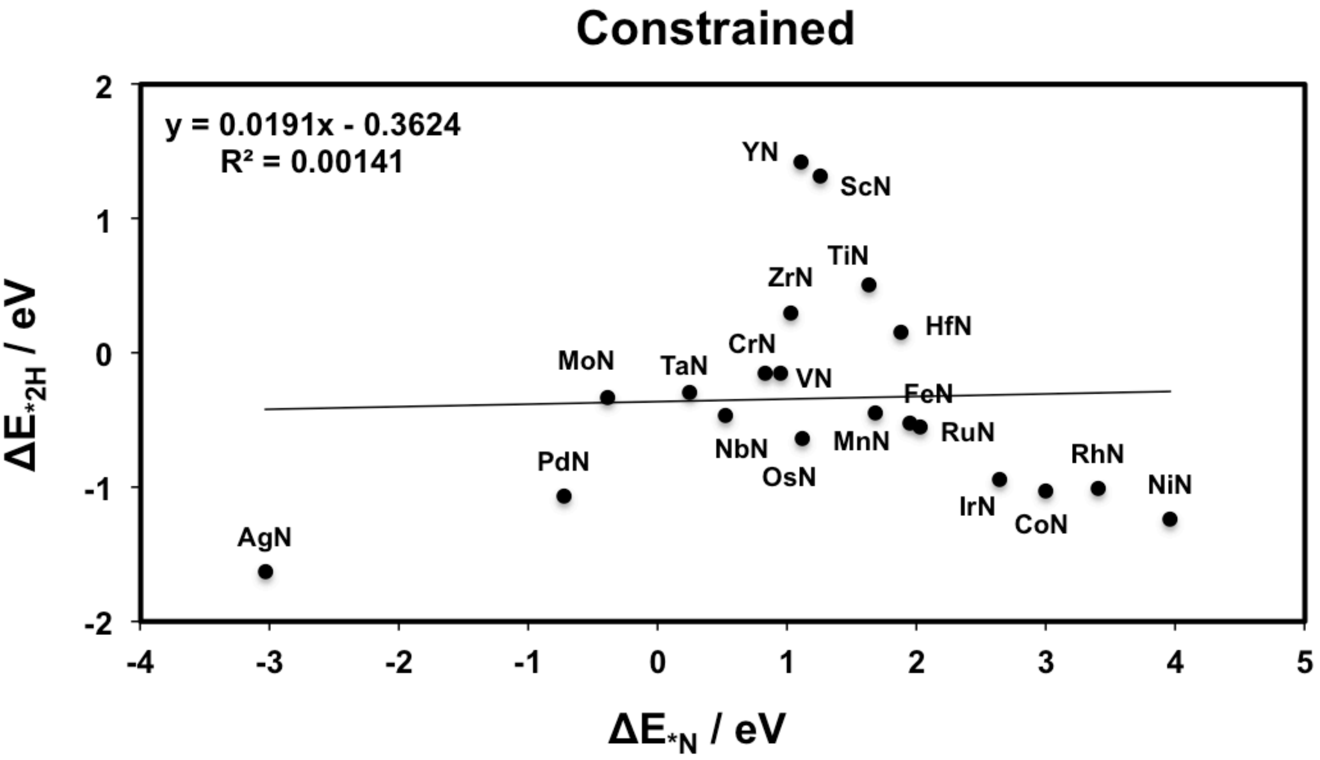
ZB (110)	**TS**	**ZPE**
NH_3	0.74	0.89
H_2	0.41	0.27
N_2	0.6	0.15
$*N_2$	0.12	0.16
$*H_{on\_M}$	0.01	0.21
$*H_{on\_N}$	0.007	0.29
***2H**	0.013	0.64
***3H**	0.05	0.96
***N**	0.07	0.08

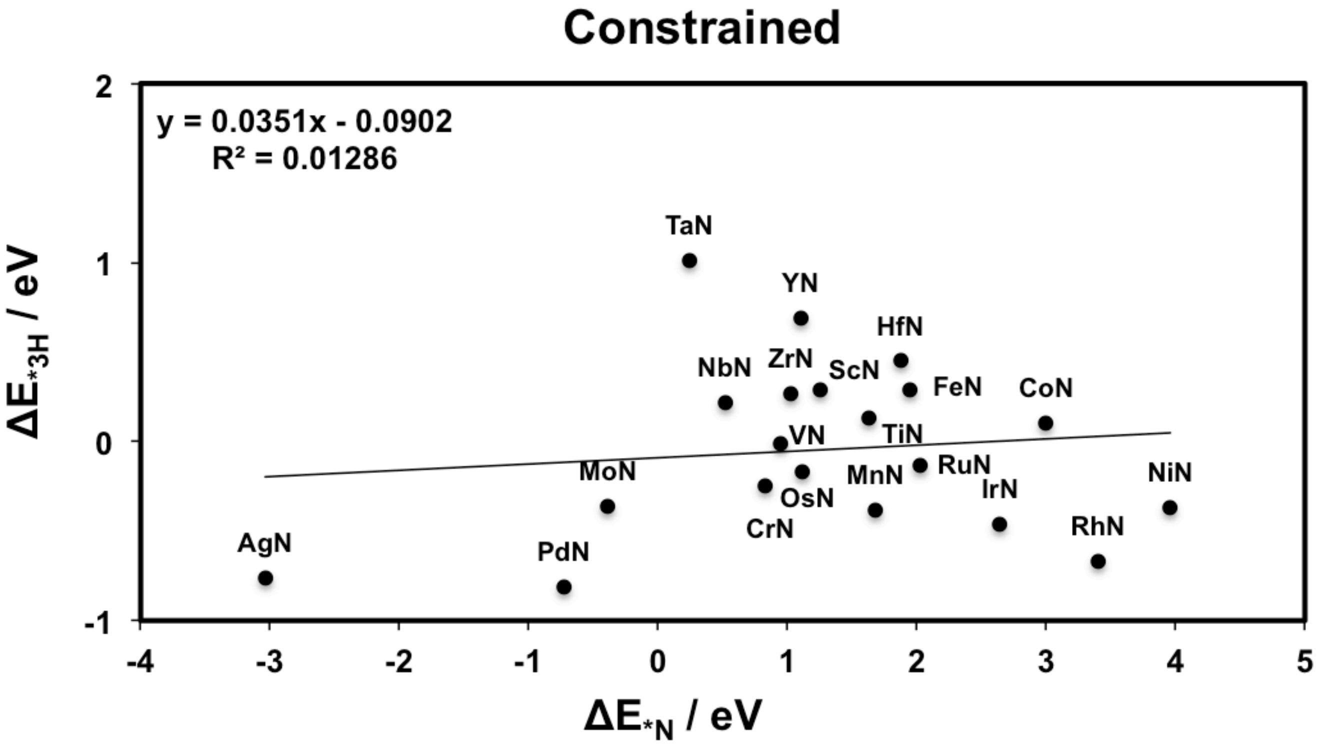
Table 4. Decomposition potentials for metal nitrides to decompose according to Eq. 27 in the article. Also included are the calculated onset potentials for electrocatalytic NH3 formation. All values are calculated at 300 K.

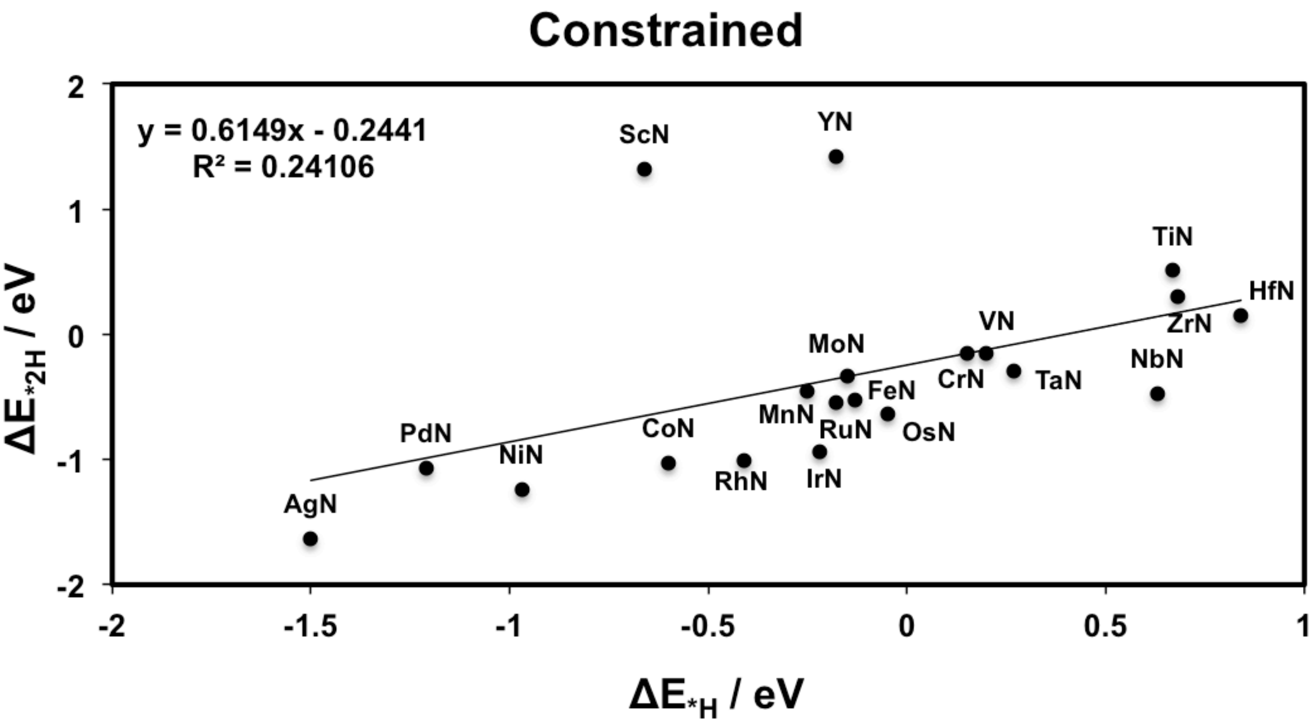
Nitride	ΔG_f / eV	ΔG (H^+/e^-) / eV	Decomposition potential / V	Onset potential / V
ZrN	-2.98	2.81	-0.94	-0.76
VN	-1.63	1.46	-0.49	-0.51
NbN	-1.49	1.32	-0.44	-0.65
CrN	-0.33	0.16	-0.05	-0.76

Upon exploring the possibility of estimating the trends in catalytic activity of transition metal nitrides in the reduction of nitrogen, it was found that nitrides span a wide range of binding energies. As shown in Fig. 2, the binding energies of species do not scale well with a single descriptor like the binding energy of *N or *H, where *N is the addition of N on a metal atom of a clean slab whereas *H is the addition of H atom on an N atom in the 1st surface layer, see Eq (5) in the paper. *2H and *3H are the second and third protonation in the catalytic cycle, see Eqs. (6) and (7) in the paper. The scaling is much better with *H as a descriptor than with *N which is expected since all the *xH species are of similar nature (H adsorbing on an N atom), whereas the *N is adsorbing on a metal atom; hence a correlation is not necessarily expected there. A few outliers are, however, observed for the *H descriptor.




Constrained
y = 0.0191x - 0.3624
R² = 0.00141
YN
ScN
TiN
ZrN
HfN
CrN
MoN
TaN
VN
FeN
NbN
MnN
RuN
OsN
PdN
RhN
NiN
IrN
CoN
AgN
ΔE*2H / eV
ΔE*N / eV
2
1
0
-1
-2
-4
-3
-2
-1
0
1
2
3
4
5


Constrained
y = 0.0351x - 0.0902
R² = 0.01286
TaN
YN
HfN
NbN
ZrN
ScN
FeN
CoN
VN
TiN
MoN
RuN
MnN
IrN
NiN
OsN
CrN
AgN
PdN
RhN
ΔE*3H / eV
ΔE*N / eV
2
1
0
-1
-4
-3
-2
-1
0
1
2
3
4
5



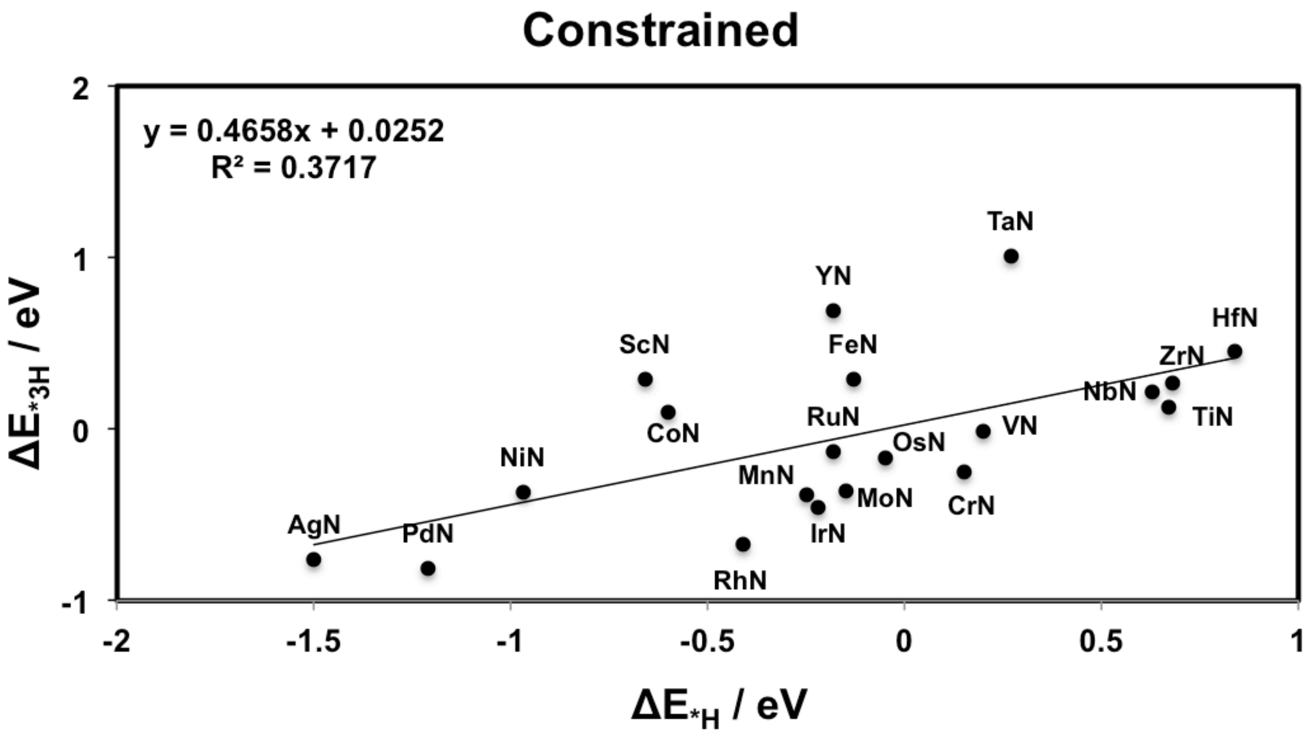
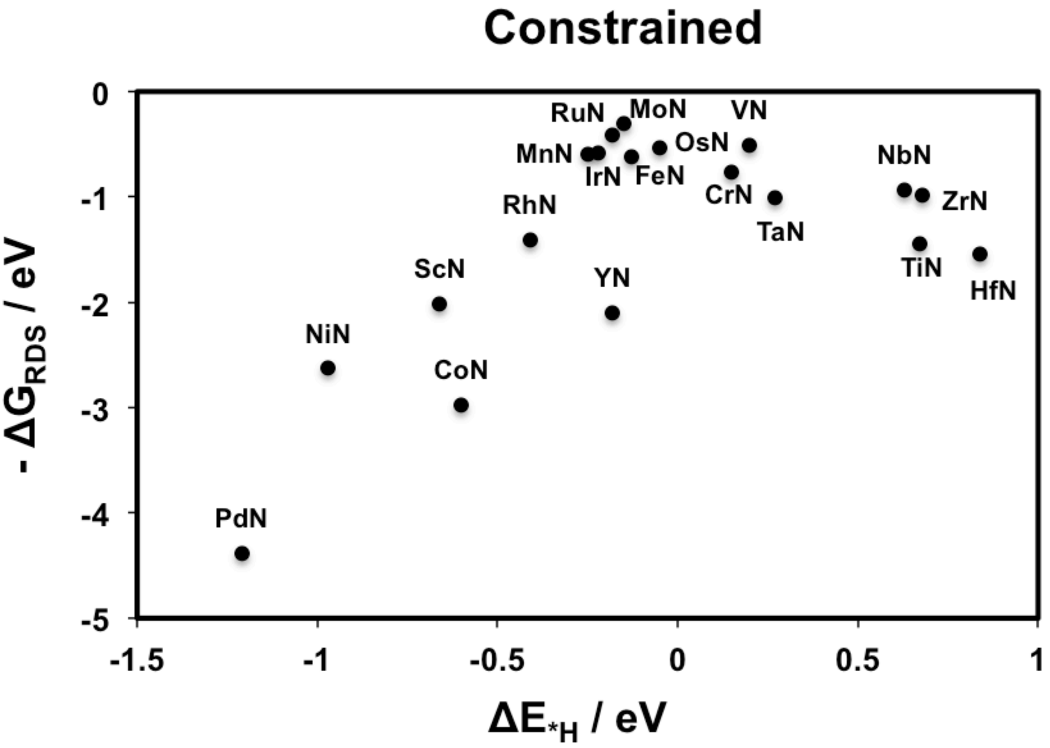
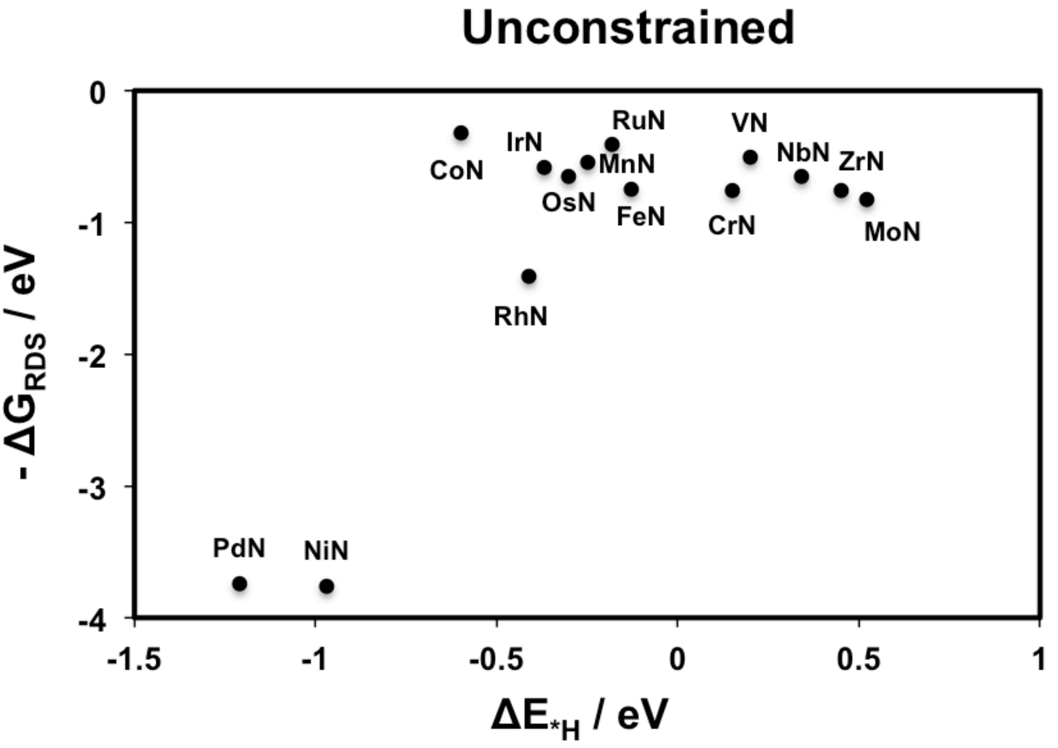
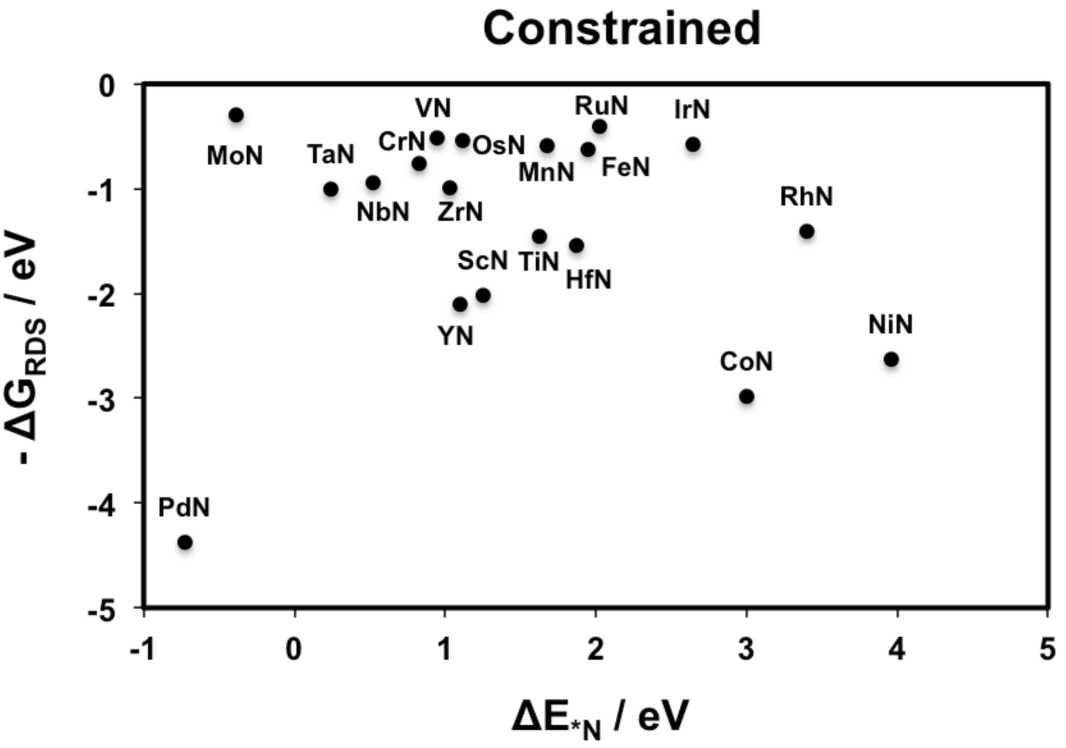


Fig 2. Adsorption energies of *H, *2H, *3H as a function of the chemisorption energy of *N or *H on transition metal nitrides. Binding energies span a wide range and departure from scaling relations is observed. Clearly, the *H binding energy is a better descriptor than *N.

The negative of the change of the free energy, -ΔG, which within our approximations gives the onset potential, is shown in Fig. 3 as a function of *H and *N for both constrained and unconstrained approach. For unconstrained pathway, the binding energy of *H does not always correspond to the first proton that adsorbs on surface. For some nitrides like ZrN and NbN, the first proton always binds strongest to a metal atom. However, the binding energy of the first H atom which binds to the surface N atom is always used, and referred to as *H. For the constrained approach, choosing *H as a single descriptor gives a better volcano-type plot compared to when *N is chosen (which is expected and explained above, in relation with Fig. 2). The volcano obtained for the unconstrained data gives also rise to a volcano plot when *H is used as a descriptor. In the paper itself, we have chosen to plot this data against the metal nitride type (in a bar chart), rather than the descriptor *H (volcano-plot). Most candidates are predicted to have high catalytic activity. However, as we show in the paper, most of them get eliminated as promising candidates for this reaction at an earlier or a later stage due to instable N-vacancy, poisoning of the N-vacancy by H or O from the solution, or because the nitride decomposes at the operating conditions. The descriptor-based analysis approach can, however, be used in future screening studies of other possible metal nitride candidates for this reaction, where *H may be used as the common descriptor.




Unconstrained
- ΔG_RDS / eV
ΔE*H / eV
0
-1
-2
-3
-4
-1.5
-1
-0.5
0
0.5
1
CoN
IrN
OsN
MnN
RuN
FeN
RhN
VN
CrN
NbN
ZrN
MoN
PdN
NiN


Constrained
- ΔG_RDS / eV
ΔE*N / eV
0
-1
-2
-3
-4
-5
-1
0
1
2
3
4
5
MoN
TaN
NbN
CrN
VN
OsN
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YN
RhN
NiN
CoN
PdN

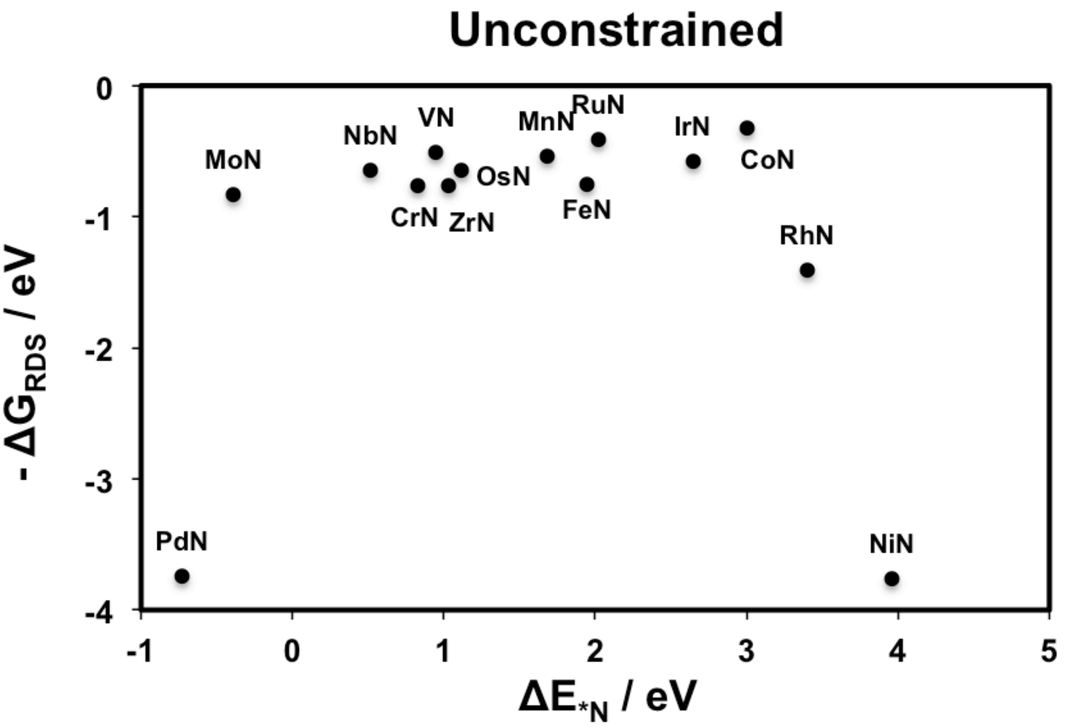

Fig 3. Negative of the change of the free energy, -ΔG, plotted as a function of *H (adsorbed on a N atom in the 1st surface layer) or *N (adsorbed on a metal atom in the 1st surface layer).

References

1. J. K. Nørskov, J. Rossmeisl, A. Logadóttir, L. Lindqvist, J. R. Kitchin, T. Bligaard, and H. Jónsson, *J. Phys. Chem. B*, 2004, **108**, 17886–17892.

2. R. C. Weast, *CRC Handbook of Chemistry and Physics*, 49th edn., p. D109, The Chemical Rubber Company, Cleveland 1968-1969.

3. P. W. Atkins, *Physical Chemistry*, Oxford University Press, 6th edn., 1998.

Table 5. Summary table of the most stable nitrides studied for electrochemical ammonia formation.

Nitride	Facet Stability	Vacancy Stability	Activity (Constrained)		Activity (Unconstrained)			Vacancy Poisoning		Potential	
		$E_{a,vac}$ (eV)	RDS	ΔG_{RDS} (eV)	RDS	ΔG_{RDS} (eV)	# H^{+}/e^{-}	$\Delta G_{(N\text{-}O)}$ (eV)	$\Delta G_{(N\text{-}H)}$ (eV)	U_{decomp} (V)	U_{onset} (V)
ZrN	RS(100)	2.69	^{A}NH	0.99	$^{A}ZrH^{A}NH$	0.76	8	-1.96	-1.55	-0.94	-0.76
VN	RS(100)	1.69	^{A}NH	0.51	^{A}NH	0.51	6	-1.22	-0.66	-0.49	-0.51
NbN	RS(100)	1.34	^{A}NH	0.94	$^{A,B}NbH^{A}NH$	0.65	8	-1.88	-0.94	-0.44	-0.65
CrN	RS(100)	1.82	$^{A}NH_{3(g)}{}^{B}NH$	0.76	$^{A}NH_{3(g)}{}^{B}NH$	0.76	6	-1.56	-0.09	-0.05	-0.76
MnN	RS(100)	1.13	$^{A}NH_{3(g)}{}^{B}NH_{2}$	0.59	$^{A,B}NH_{2}{}^{C}NH^{D}NH_{2}$	0.54	9	-0.97	0.26		
MoN	RS(100)	1.03	$^{A}NH_{3(g)}{}^{B}NH$	0.30	$^{A\text{-}D}MoH^{A}NH$	0.83	12	-2.12	0.08		
RuN	ZB(110)	1.42	$^{B}NH_{3(g)}$	0.41	$^{B}NH_{3(g)}$	0.41	6	-0.324	0.57		
OsN	ZB(110)	1.34	$^{A}NH_{3(g)}$	0.53	$^{A\text{-}D}OsH^{B}NH^{D}NH_{2}$ $^{A,C}NH_{3(g)}{}^{A,C}N$	0.65	13	-1.96	0.13		
TiN	RS(100)	3.03	$^{A}NH_{3(g)}{}^{B}NH_{2}$	1.45	H_2 formation						
TaN	RS(100)	1.01	$^{A}NH_{3}$	1.01	H_2 formation						
HfN	RS(100)	2.73	$^{A}NH_{3}$	1.54							
YN	RS(100)	2.93	$^{A}NH_{3(g)}{}^{B}NH_{2}$	2.10							
ScN	RS(100)	2.75	$^{A}NH_{3(g)}{}^{B}NH_{2}$	2.02							
RhN	ZB(110)	0.56	$^{A,B}NH_{3(g)}{}^{A,B}N$	1.41							
FeN	ZB(110)	0.90									
PdN	ZB(110)	0.43									
AgN	RS(100)	0.43									
CoN	ZB(110)	0.49									
CuN	RS(100)	0.50									
NiN	ZB(110)	0.28									
IrN	ZB(110)	0.79									