Electronic Supplementary Material (ESI)

Impact of Dopant-induced Ensemble Structure of Hetero Double Atom Catalysts in Electrochemical NH_3 Production

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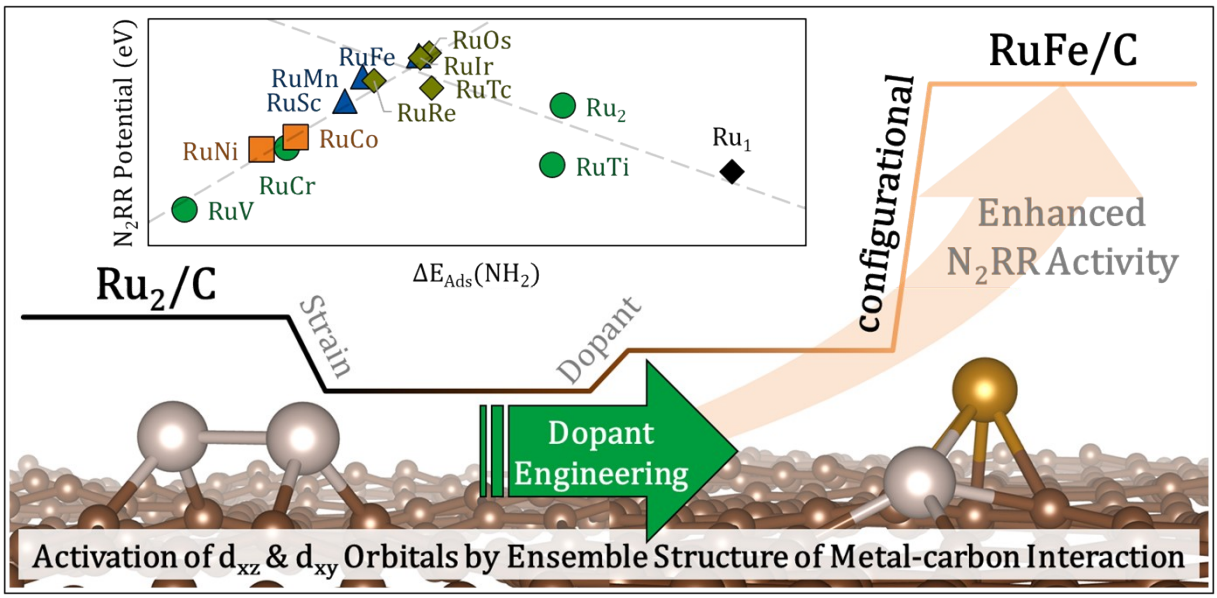
Graphical Abstract



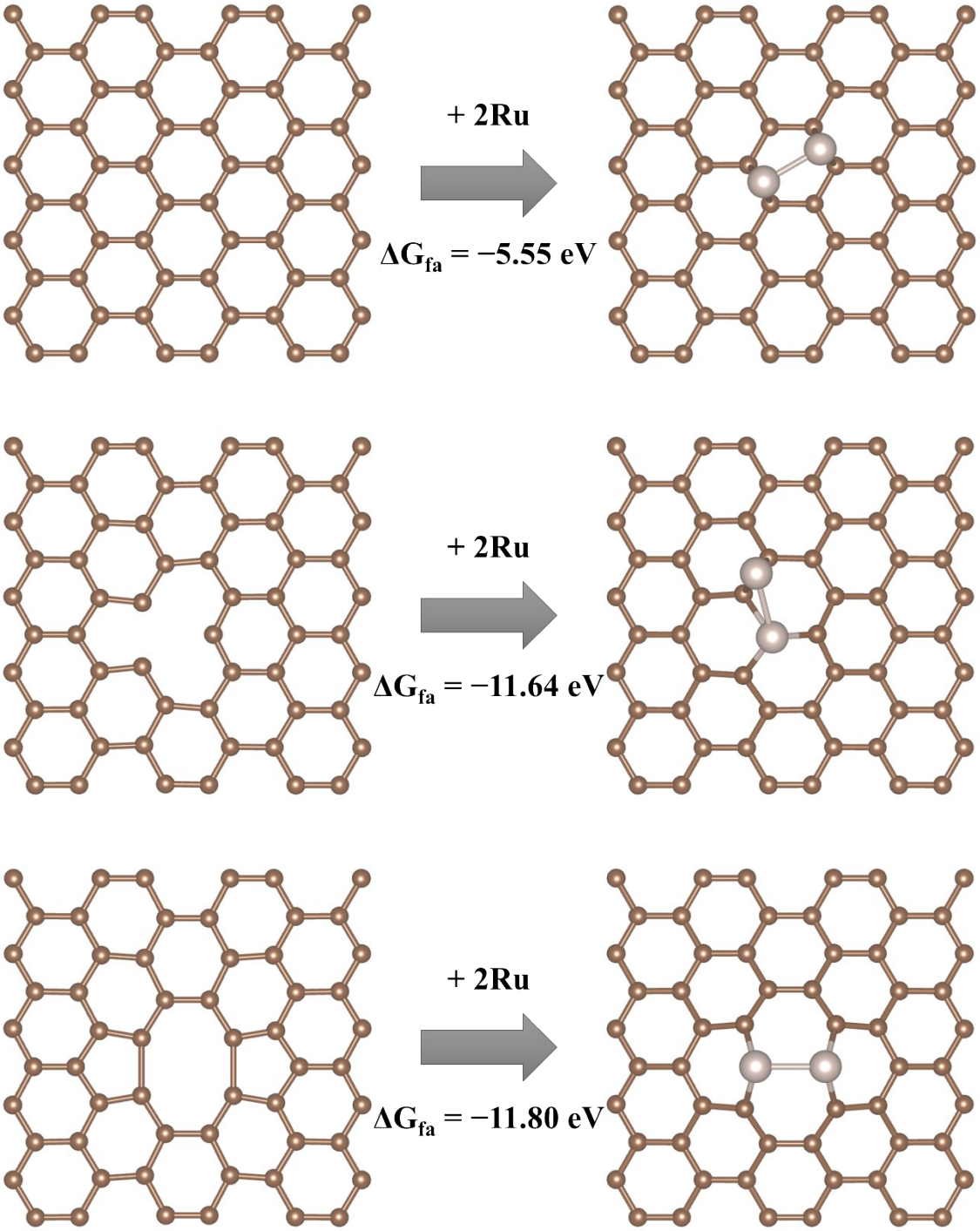


Figure S1 Formation energy of homo Ru DAC on pristine graphene (upper), defective graphene with single vacancy (middle), and defective graphene with double vacancies (bottom)

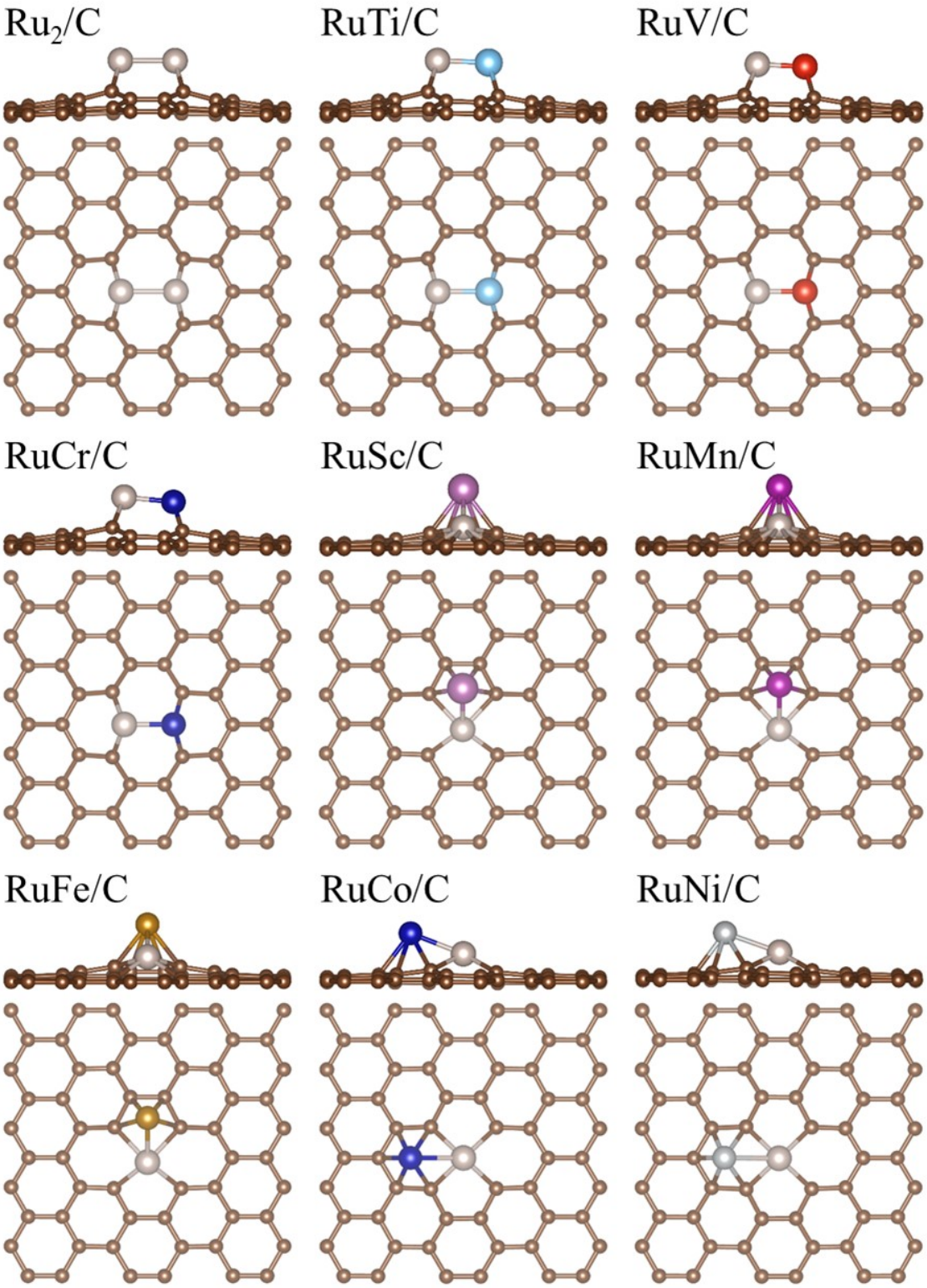


Figure S2 Optimized ensemble geometries of homo Ru DAC and hetero RuM DACs

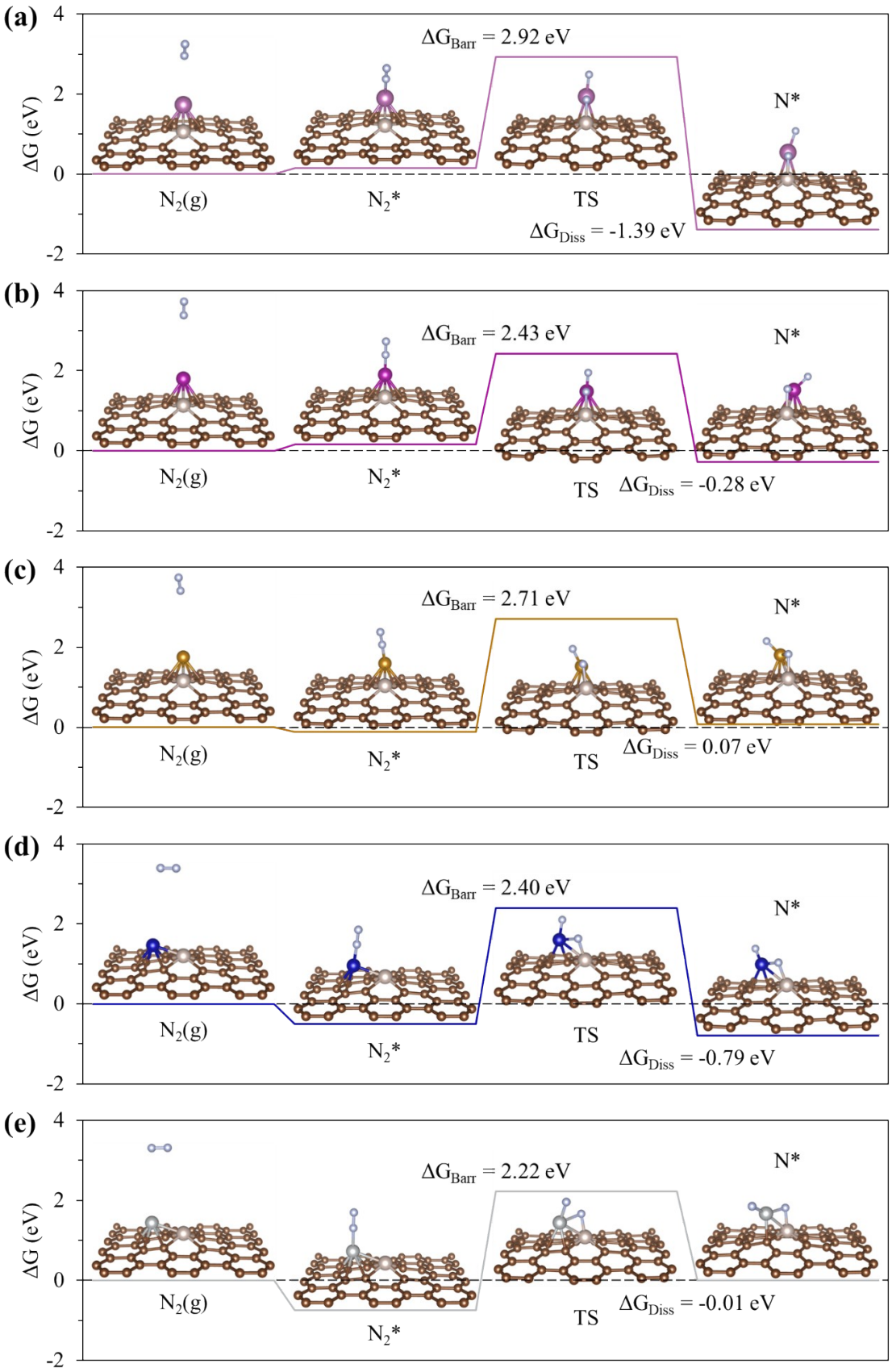

(a)
ΔG_Barr = 2.92 eV
N*
N2(g)
N2*
TS
ΔG_Diss = -1.39 eV
(b)
ΔG_Barr = 2.43 eV
N*
N2(g)
N2*
TS
ΔG_Diss = -0.28 eV
(c)
ΔG_Barr = 2.71 eV
N*
N2(g)
N2*
TS
ΔG_Diss = 0.07 eV
(d)
ΔG_Barr = 2.40 eV
N*
N2(g)
N2*
TS
ΔG_Diss = -0.79 eV
(e)
ΔG_Barr = 2.22 eV
N*
N2(g)
N2*
TS
ΔG_Diss = -0.01 eV
ΔG (eV)
4
2
0
-2

Figure S3 N_2 dissociation energy (ΔG_{Diss}) and barrier (ΔG_{Barr}) for (a) RuSc/C, (b) RuMn/C, (c) RuFe/C, (d) RuCo/C, and (e) RuNi/C

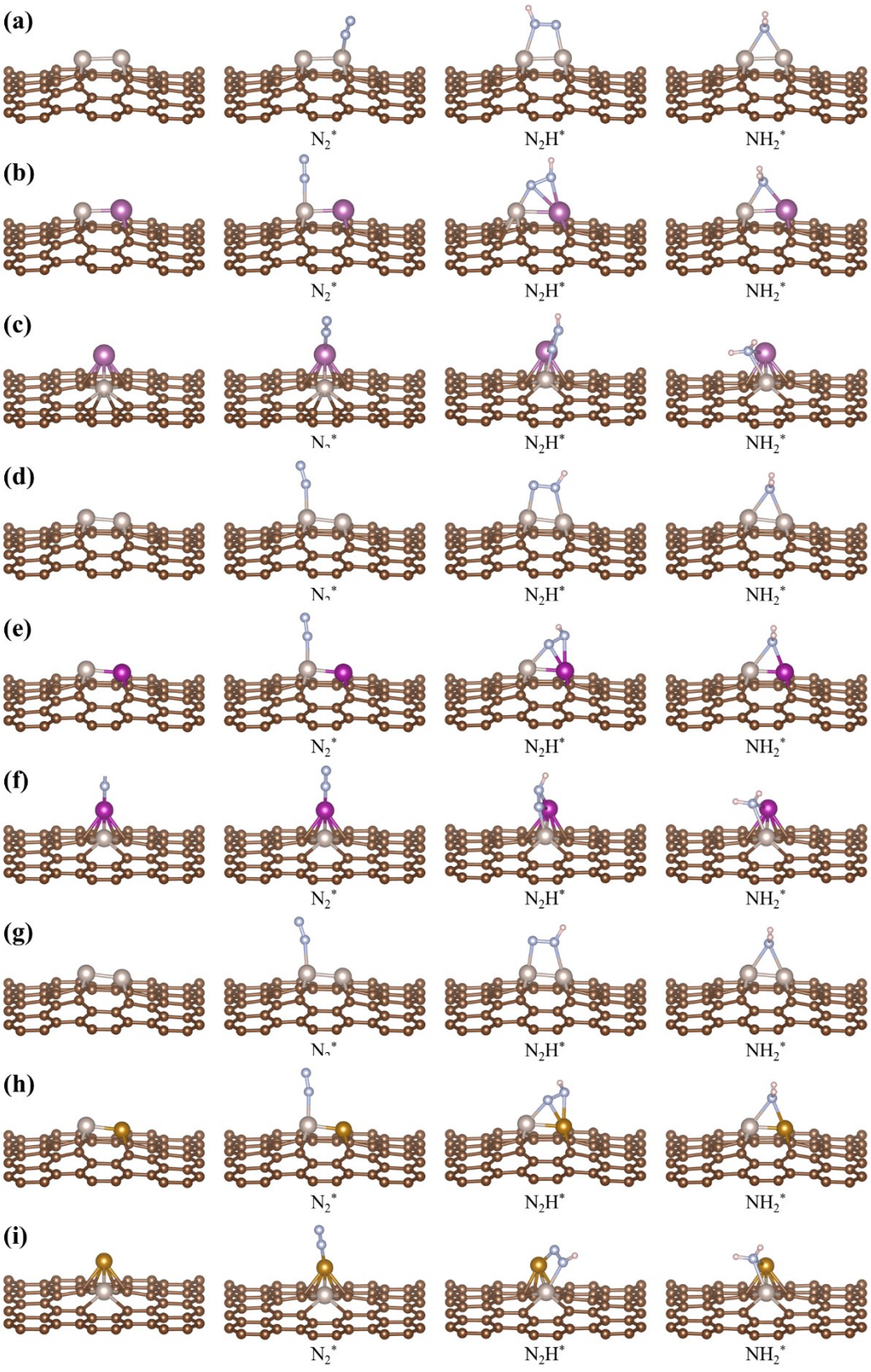
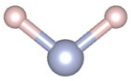
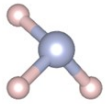
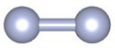
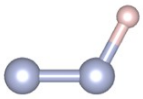
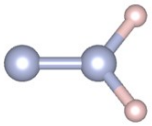
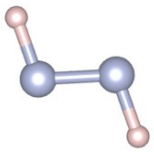


Figure S4 Optimized geometry of hetero RuM DACs in group II with progressively added strain, dopant and configurational effects. (a) $RuSc_{strained}$, (b) $RuSc_{doped}$, (c) RuSc/C, (d) $RuMn_{strained}$, (e)

$RuMn_{doped}$, (f) RuMn/C, (g) $RuFe_{strained}$, (h) $RuFe_{doped}$, and (i) RuFe/C. In this figure, the bare surface, N_2*, N_2H* and NH_2* are shown sequentially from the left column.

Table S1 Calculated total energy of N_2RR intermediates

X	N	NH	NH_2	NH_3
Configuration				
E_X (eV)	−3.11	−8.09	−13.52	−19.52

X	N_2	N_2H	N_2H_2	HN_2H
Configuration				
E_X (eV)	−16.61	−18.00	−21.12	−22.04

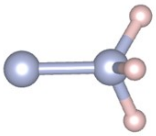
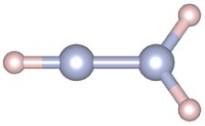
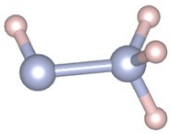
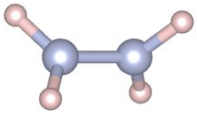
X	N_2H_3	HN_2H_2	HN_2H_3	$H_2N_2H_2$
Configuration				
E_X (eV)	−22.96	−23.79	−28.39	−29.97

Table S2 Calculated adsorption energy of N_2H and NH_2 on the Ru SAC, homo Ru DAC, and hetero RuM DACs.

(eV)	Ru_1/C	Group I				Group II			Group III	
		Ru_2/C	RuTi/C	RuV/C	RuCr/C	RuSc/C	RuMn/C	RuFe/C	RuCo/C	RuNi/C

$\Delta E_{Ads}(N_2H)$	−1.64	−2.21	−2.11	−2.61	−2.96	−3.39	−2.77	−2.77	−3.32	−2.88
$\Delta E_{Ads}(NH_2)$	−2.96	−3.32	−3.34	−4.12	−3.90	−3.78	−3.74	−3.62	−3.89	−3.96

Table S3 Potential limiting step, onset potential and adsorption energy of NH_2 and N_2H on the RuM DACs with progressively added strain, dopant, and configurational effects.

	Limiting Step	**Onset Potential (V)**	**$\Delta E_{Ads}(N_2)$ (eV)**	**$\Delta E_{Ads}(N_2H)$ (eV)**	**$\Delta E_{Ads}(NH_2)$ (eV)**
Ru_2/C	$N_2^* + (H^+ + e^-) \rightarrow N_2H^*$	−0.91	−0.84	−2.21	−3.32
$RuSc_{strained}$	$N_2^* + (H^+ + e^-) \rightarrow N_2H^*$	−1.19	−1.10	−2.21	−3.38
$RuSc_{doped}$	$NH_2^* + (H^+ + e^-) \rightarrow NH_3$	−0.46	−1.12	−3.15	−3.29
RuSc/C	$NH_2^* + (H^+ + e^-) \rightarrow NH_3$	−0.89	−0.52	−3.39	−3.78
$RuMn_{strained}$	$N_2^* + (H^+ + e^-) \rightarrow N_2H^*$	−0.91	−0.80	−2.20	−3.25
$RuMn_{doped}$	$N_2^* + (H^+ + e^-) \rightarrow N_2H^*$	−0.78	−0.54	−2.10	−3.49
RuMn/C	$NH_2^* + (H^+ + e^-) \rightarrow NH_3$	−0.81	−0.89	−2.77	−3.74
$RuFe_{strained}$	$N_2^* + (H^+ + e^-) \rightarrow N_2H^*$	−0.97	−0.83	−2.22	−3.30
$RuFe_{doped}$	$N_2^* + (H^+ + e^-) \rightarrow N_2H^*$	−0.78	−0.57	−2.26	−3.66
RuFe/C	$N_2^* + (H^+ + e^-) \rightarrow N_2H^*$	−0.73	−1.15	−2.77	−3.62

Table S4 Calculated formation energy of further screened hetero RuM DACs. Bold text on each catalyst indicates the most stable geometry.

ΔE_f (eV)		**c1**	**c2**	**c3**	**c4**	**c5**	**c6**	**c7**	**c8**	**c9**
3d	RuCu/C	-†	0.09	0.25	0.24	-†	-1.10	**-1.69**	-†	-†
	RuZn/C	4.83	3.10	3.03	2.48	4.16	-0.01	**-0.54**	-†	-†
4p	RuGa/C	2.93	0.60	-†	-0.43	-†	-2.07	-1.71	**-2.17**	-2.03
	RuGe/C	1.10	-0.24	-†	-2.27	-2.87	-2.34	-2.27	**-2.90**	-2.37
	RuAs/C	1.25	0.38	-†	-2.14	0.02	**-2.44**	-2.41	-†	-†
4d	RuY/C	3.56	-†	-†	0.01	1.40	**-1.83**	-0.08	-1.90	-1.78
	RuZr/C	-1.60	-3.18	-2.76	-4.88	-2.83	-4.82	-3.17	**-5.00**	-4.91
	RuNb/C	-2.54	-3.77	-3.38	**-4.81**	-2.60	-3.99	-2.68	-3.85	-4.11

	RuMo/C	-2.11	-2.92	-2.29	**-3.30**	-1.71	-2.37	-2.00	-2.40	-2.64
	RuTc/C	-3.13	-3.61	-3.23	**-3.98**	-2.38	-3.06	-3.09	-3.14	-3.34
	RuRh/C	-1.64	-2.51	-2.60	-3.04	-1.17	-3.05	-2.90	**-3.20**	-3.18
	RuPd/C	1.80	0.34	0.05	-0.40	-†	-1.70	-1.86	**-1.90**	-1.83
	RuAg/C	4.80	2.55	2.81	2.35	3.75	-0.52	**-1.19**	-†	-†
	RuCd/C	7.13	-†	-†	3.38	4.31	-0.01	**-0.47**	-†	-†
5p	RuIn/C	4.40	-†	-†	1.36	2.90	-1.87	-1.47	**-1.91**	-1.82
	RuSn/C	2.52	-†	-†	-0.44	1.30	-2.00	-1.96	**-2.57**	-2.10
	RuSb/C	2.37	1.83	-†	-0.85	1.02	-1.08	**-1.82**	-1.00	-†
5d	RuHf/C	-2.03	-3.53	-3.08	-5.15	-3.12	-4.74	-3.58	**-5.16**	-4.94
	RuTa/C	-4.16	-5.18	-4.83	**-6.10**	-3.72	-4.77	-3.92	-4.89	-4.72
	RuW/C	-4.34	-4.88	-4.28	**-4.91**	-3.18	-3.53	-2.91	-3.42	-3.59
	RuRe/C	-3.72	**-4.06**	-3.63	-3.92	-2.32	-2.56	-2.53	-2.34	-2.57
	RuOs/C	-4.38	-4.45	**-4.50**	-4.25	-2.57	-3.31	-3.26	-2.85	-3.18
	RuIr/C	-3.65	**-4.11**	-4.04	-3.95	-1.96	-3.13	-3.54	-3.05	-2.98
	RuPt/C	-1.19	-2.27	-2.29	-2.42	-0.30	-2.25	**-3.37**	-2.67	-†
	RuAu/C	2.73	1.11	1.20	1.32	2.55	-0.60	**-2.16**	-†	-†
	RuHg/C	6.93	5.95	3.77	3.77	4.45	-0.01	**-0.36**	-†	-†
6p	RuTl/C	6.00	3.04	1.70	1.70	3.04	**-1.80**	-1.42	-1.79	-1.73
	RuPb/C	4.20	2.09	0.63	0.49	2.52	-1.80	-1.79	**-2.38**	-1.98
	RuBi/C	4.13	1.70	0.04	0.04	-1.38	-0.80	**-1.57**	-1.38	-†

† Those geometries are too unstable to be applicable.

Table S5 Onset potential of N_2RR, HER, and the difference between two onset potentials on the additional candidates for hetero RuM DACs.

(eV)	RuTc/C	RuRe/C	RuOs/C	RuIr/C
ΔG_{NRR}	−0.84	−0.82	−0.72	−0.74
ΔG_{HER}	−0.46	−0.19	−0.43	−0.07

ΔΔG	−0.38	−0.63	−0.29	−0.67