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Understanding Trends in Activity and Selectivity of Bi-atom Catalysts for Electrochemical Reduction of Carbon Dioxide

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Table S1. The distances between the central metal atoms ($d_{M\text{-}M}$) in homo-nuclear BACs and the distance between two adjacent atoms in bulk metal ($b_{M\text{-}M}$), unit in angstrom (Å).

Species	Bulk	BACs
Ag	2.89	2.77
Al	2.86	2.59
Au	2.88	2.70
Ca	3.95	3.08
Co	2.50	2.25
Cr	2.50	2.28
Cu	2.56	2.62
Fe	2.48	2.22
Hf	3.13	2.98
Ir	2.72	2.38
Mg	3.20	2.63
Mo	2.73	2.38
Nb	2.86	2.54
Ni	2.49	2.57
Os	2.68	2.35
Pd	2.75	2.63
Pt	2.78	2.69
Re	2.74	2.35
Rh	2.69	2.36

Ru	2.65	2.33
Sc	3.25	2.95
Sn	2.81	3.40
Sr	4.30	3.27
Ta	2.86	2.59
Ti	2.89	2.61
W	2.74	2.41
Y	3.56	3.26
Zn	2.67	2.57
Zr	3.18	2.96
Mn	2.28	2.27
Ga	2.53	2.67
Bi	3.10	3.45

Table S2. The number of electrons (n_e) involved in the dissolution for the pure metals, standard dissolution potentials ($U^0_{diss(metal)}$, pH = 0), energy of central metal atom (E_M), the formation energy, E_f, and computed dissolution potentials (U_{diss}) for SACs. Some of them refers from the publication of Guo et al.[1]

Species	n_e	$U^0_{diss(metal)}$ (V)	E_M (eV)	E_f (eV)	U_{diss} (V)
Ag	1	0.80	-2.83	-0.23	1.03
Al	3	-1.66	-3.75	-5.04	0.02
Au	3	1.50	-3.90	-0.09	1.53
Bi	1	0.50	-3.90	-1.58	2.08
Ca	2	-2.89	-1.96	-4.36	-0.71
Co	2	-0.28	-7.11	-3.39	1.41
Cr	2	-0.91	-9.64	-3.67	0.92
Cu	2	0.34	-4.10	-1.69	1.19
Fe	2	-0.45	-8.46	-3.50	1.30

Ga	3	-0.55	-3.04	-2.58	0.31
Hf	4	-1.55	-9.95	-4.20	-0.50
Ir	3	1.16	-8.86	-2.38	1.95
Mg	2	-2.37	-0.55	-4.78	0.02
Mn	2	-1.19	-9.16	-3.96	0.79
Mo	3	-0.20	-10.86	-2.41	0.60
Nb	3	-1.10	-10.11	-3.27	-0.01
Ni	2	-0.26	-5.78	-2.95	1.22
Os	8	0.84	-11.22	-2.20	1.11
Pd	2	0.95	-5.18	-2.06	1.98
Pt	2	1.18	-6.06	-2.11	2.24
Re	3	0.30	-12.44	-2.15	1.02
Rh	2	0.60	-7.36	-2.76	1.98
Ru	2	0.46	-9.28	-2.65	1.78
Sc	3	-2.08	-6.34	-5.31	-0.31
Sn	2	-0.14	-4.01	-2.12	0.92
Sr	2	-2.90	-1.69	-8.62	1.41
Ta	3	-0.60	-11.86	-2.88	0.36
Ti	2	-1.63	-7.90	-4.32	0.53
V	2	-1.18	-9.09	-3.73	0.68
W	3	0.10	-12.96	-2.44	0.91
Y	3	-2.37	-6.47	-7.33	0.07

Zn	2	-0.76	-1.27	-2.16	0.32
Zr	4	-1.45	-8.55	-3.90	-0.48

Table S3. The detailed electronic energy (E_*) and binding energy (E) of critical intermediates (*CO_2, *COOH, *CO, and *HCOO) in homonuclear BACs during electrochemical CO_2RR.

Species	E_*	E_{*CO_2}	E_{CO_2}	E_{*COOH}	E_{COOH}	E_{*CO}	E_{CO}	E_{*HCOO}	E_{HCOO}
Bi-Bi	-513.98	-537.05	-0.11	-539.23	0.90	-528.85	0.21	-539.89	-0.21
Co-Co	-524.01	-547.09	-0.12	-549.87	0.30	-538.89	0.19	-549.55	0.46
Cr-Cr	-529.64	-552.73	-0.13	-556.79	-1.00	-545.98	-1.27	-556.83	-1.72
Cu-Cu	-514.60	-537.78	-0.22	-539.71	1.04	-529.48	0.20	-540.04	0.51
Fe-Fe	-526.94	-550.02	-0.13	-553.23	-0.13	-542.46	-0.45	-552.87	-0.21
Ga-Ga	-514.30	-537.41	-0.15	-541.04	-0.59	-529.31	0.07	-541.70	-1.64
Ir-Ir	-525.50	-548.62	-0.16	-551.46	0.19	-540.21	0.36	-550.72	1.01
MnMn	-529.26	-552.33	-0.11	-555.94	-0.53	-545.38	-1.05	-555.84	-0.72
MoMo	-529.56	-552.61	-0.10	-556.66	-0.95	-546.11	-1.48	-557.36	-2.63
Ni-Ni	-520.48	-543.57	-0.13	-545.81	0.83	-535.36	0.20	-545.75	0.93
Os-Os	-529.85	-552.96	-0.16	-556.77	-0.77	-545.98	-1.05	-556.13	1.01
Pd-Pd	-517.50	-540.81	-0.36	-543.22	0.43	-532.57	0.00	-542.61	0.91
Pt-Pt	-519.36	-542.70	-0.39	-545.30	0.22	-534.46	-0.03	-544.40	1.04
Re-Re	-532.17	-555.26	-0.12	-559.01	-0.68	-548.92	-1.67	-559.27	-0.31
Rh-Rh	-523.25	-546.35	-0.14	-548.84	0.56	-538.13	0.20	-548.52	1.03
Ru-Ru	-526.87	-549.98	-0.15	-553.65	-0.62	-542.78	-0.83	-553.15	0.09

Sn-Sn	-515.29	-538.35	-0.11	-541.39	0.05	-530.13	0.23	-541.78	-0.14
Sr-Sr	-524.23	-547.51	-0.33	-549.92	0.46	-539.27	0.03	-551.25	-1.40
Ta-Ta	-532.50	-557.13	-1.67	-560.22	-1.57	-549.02	-1.44	-561.58	-4.06
Ti-Ti	-527.46	-551.27	-0.85	-554.67	-1.05	-543.47	-0.93	-556.11	-3.57
V-V	-528.66	-551.85	-0.24	-555.55	-0.74	-544.83	-1.10	-556.80	-3.19
W-W	-533.81	-556.88	-0.12	-560.49	-0.52	-549.76	-0.88	-561.27	-2.14
Zn-Zn	-509.88	-532.96	-0.12	-535.59	0.44	-524.73	0.22	-536.06	-0.40
Ag-Ag	-509.14								
Al-Al	-520.60								
Au-Au	-511.00								
Ca-Ga	-515.65								
Hf-Hf	-531.33								
MgMg	-513.68								
Nb-Nb	-529.77								
Sc-Sc	-526.32								
Y-Y	-530.61								
Zr-Zr	-527.91								

Table S4. The detailed electronic energy (E_*) and binding energy (E) of critical intermediates (*CO_2, *COOH, *CO, *H, and *HCOO) in Mo-based heteronuclear BACs during electrochemical CO_2RR.

Species	Mo-Fe	Mo-Co	Mo-Ir	Mo-Rh	Mo-Ni	Mo-Cu	Mo-Zn	Mo-Ga
E_*	-528.60	-527.34	-528.41	-527.17	-525.25	-522.24	-520.01	-521.30

E_{*CO2}	-552.32	-550.52	-551.50	-550.26	-548.32	-545.31	-543.23	-545.26
E_{CO_2}	-0.76	-0.23	-0.13	-0.13	-0.11	-0.11	-0.26	-1.00
E_{*COOH}	-555.45	-553.26	-554.37	-552.72	-550.65	-548.15	-546.62	-548.11
E_{COOH}	-0.70	0.23	0.20	0.60	0.76	0.25	-0.46	-0.65
E_{*CO}	-545.16	-543.94	-544.98	-543.74	-541.96	-538.95	-536.67	-537.90
E_{CO}	-1.48	-1.53	-1.50	-1.50	-1.63	-1.63	-1.59	-1.51
E_{*H}	-532.59	-531.49	-532.54	-531.31	-529.44	-526.42	-524.13	-525.35
E_{H}	-0.54	-0.71	-0.69	-0.69	-0.74	-0.73	-0.68	-0.59
E_{*HCOO}	-556.41	-555.16	-556.17	-554.97	-553.09	-550.05	-548.07	-549.63
E_{HCOO}	-1.65	-1.67	-1.61	-1.64	-1.68	-1.65	-1.91	-2.17

Table S5. The detailed electronic energy (E_*) and binding energy (E) of critical intermediates (*CO_2, *COOH, *CO, *H, and *HCOO) in Ta-based heteronuclear BACs during electrochemical CO_2RR.

Species	Ta-Fe	Ta-Co	Ta-Ir	Ta-Rh	Ta-Ni	Ta-Cu	Ta-Zn	Ta-Ga
E_*	-530.26	-529.04	-530.08	-528.89	-527.40	-524.33	-522.05	-523.37
E_{*CO2}	-555.00	-553.49	-554.35	-553.14	-551.98	-548.93	-546.63	-548.28
E_{CO_2}	-1.79	-1.50	-1.31	-1.30	-1.63	-1.64	-1.62	-1.95
E_{*COOH}	-558.23	-556.09	-556.93	-555.51	-553.46	-551.29	-549.28	-550.89
E_{COOH}	-1.82	-0.89	-0.69	-0.47	0.29	-0.81	-1.07	-1.36
E_{*CO}	-546.77	-545.69	-546.80	-545.56	-543.91	-540.90	-538.64	-539.96
E_{CO}	-1.44	-1.57	-1.64	-1.59	-1.43	-1.49	-1.51	-1.51
E_{*H}	-534.89	-533.68	-534.66	-533.44	-532.06	-528.98	-526.66	-527.93

E_{H}	-1.19	-1.19	-1.12	-1.10	-1.22	-1.20	-1.16	-1.11
E_{*HCOO}	-559.22	-558.05	-559.02	-557.82	-556.39	-553.29	-550.93	-552.51
E_{HCOO}	-2.81	-2.86	-2.78	-2.77	-2.84	-2.80	-2.73	-2.99

Table S6. The detailed electronic energy (E_*) and binding energy (E) of critical intermediates (*CO_2, *COOH, *CO, *H, and *HCOO) in V-based heteronuclear BACs during electrochemical CO_2RR.

Species	V-Fe	V-Co	V-Ir	V-Rh	V-Ni	V-Cu	V-Zn	V-Ga
E_*	-528.40	-527.11	-528.09	-526.82	-525.46	-522.25	-519.85	-521.41
E_{*CO2}	-552.25	-550.86	-551.78	-550.48	-548.54	-545.31	-542.94	-545.31
E_{CO_2}	-0.89	-0.79	-0.73	-0.70	-0.12	0.10	-0.13	-0.94
E_{*COOH}	-555.76	-553.71	-554.64	-553.21	-551.20	-548.14	-546.57	-548.51
E_{COOH}	-1.21	-0.45	-0.39	-0.23	0.61	0.47	-0.56	-0.94
E_{*CO}	-544.52	-543.47	-544.46	-543.16	-541.62	-538.45	-536.07	-537.60
E_{CO}	-1.05	-1.28	-1.29	-1.26	-1.08	-1.12	-1.14	-1.11
E_{*H}	-532.00	-530.78	-531.70	-530.43	-529.17	-525.94	-523.52	-525.08
E_{H}	-0.15	-0.22	-0.17	-0.16	-0.26	-0.24	-0.22	-0.22
E_{*HCOO}	-556.45	-554.82	-555.78	-554.54	-553.24	-550.06	-548.03	-550.04
E_{HCOO}	-1.89	-1.56	-1.53	-1.56	-1.63	-1.65	-2.03	-2.48

Table S7. The detailed electronic energy (E_*) and binding energy (E) of critical intermediates (*CO_2, *COOH, *CO, *H, and *HCOO) in Ti-based heteronuclear BACs during electrochemical CO_2RR.

Species	Ti-Fe	Ti-Co	Ti-Ir	Ti-Rh	Ti-Ni	Ti-Cu	Ti-Zn	Ti-Ga

E_*	-527.65	-526.44	-527.47	-526.20	-524.82	-521.65	-519.31	-520.88
E_{*CO2}	-551.90	-550.64	-551.55	-550.25	-548.30	-545.17	-542.83	-545.19
E_{CO_2}	-1.30	-1.25	-1.12	-1.09	-0.52	-0.57	-0.56	-1.35
E_{*COOH}	-555.39	-553.70	-554.67	-553.22	-551.01	-548.03	-546.29	-548.53
E_{COOH}	-1.59	-1.11	-1.04	-0.86	0.17	-0.23	-0.83	-1.50
E_{*CO}	-543.54	-542.36	-543.35	-542.09	-540.83	-537.65	-535.32	-537.04
E_{CO}	-0.82	-0.85	-0.80	-0.81	-0.93	-0.93	-0.94	-1.09
E_{*H}	-531.15	-529.99	-530.94	-529.61	-528.56	-525.37	-523.02	-524.91
E_H	-0.06	-0.10	-0.02	0.04	-0.29	-0.27	-0.27	-0.59
E_{*HCOO}	-555.74	-554.57	-555.56	-554.34	-553.15	-549.99	-547.84	-550.09
E_{HCOO}	-1.89	-1.56	-1.53	-1.56	-1.63	-1.65	-2.03	-2.48

Table S8. The detailed electronic energy (E_*) and binding energy (E) of critical intermediates (*CO_2, *COOH, *CO, *H, and *HCOO) in Cr-based heteronuclear BACs during electrochemical CO_2RR.

Species	Cr-Fe	Cr-Co	Cr-Ir	Cr-Rh	Cr-Ni	Cr-Cu	Cr-Zn	Cr-Ga
E_*	-528.19	-526.94	-527.81	-526.56	-524.73	-521.57	-519.20	-521.30
E_{*CO2}	-551.38	-550.04	-550.92	-549.67	-547.83	-544.67	-542.30	-544.41
E_{CO_2}	-0.23	-0.14	-0.15	-0.14	-0.14	-0.14	-0.14	-0.15
E_{*COOH}	-554.77	-552.72	-553.73	-552.32	-549.94	-546.68	-545.34	-548.00
E_{COOH}	-0.43	0.37	0.23	0.40	0.95	1.05	0.01	-0.54
E_{*CO}	-544.63	-543.49	-544.41	-543.12	-541.52	-538.29	-535.88	-537.47
E_{CO}	-1.05	-0.88	-0.91	-0.89	-0.88	-0.91	-1.00	-0.87

E_{*H}	-532.04	-530.88	-531.81	-530.53	-528.89	-525.65	-523.21	-524.66
E_{H}	-0.10	0.10	0.06	0.07	0.12	0.10	0.05	0.31
E_{*HCOO}	-555.99	-554.40	-555.23	-553.98	-552.52	-549.32	-547.44	-549.59
E_{HCOO}	-1.34	-0.71	-0.66	-0.67	-0.80	-0.86	-1.47	-1.91

Table S9. The detailed electronic energy (E_*) and binding energy (E) of critical intermediates (*CO_2, *COOH, *CO, *H, and *HCOO) in Mn-based heteronuclear BACs during electrochemical CO_2RR.

Species	Mn-Fe	Mn-Co	Mn-Ir	Mn-Rh	Mn-Ni	Mn-Cu	Mn-Zn	Mn-Ga
E_*	-528.19	-526.94	-527.81	-526.56	-524.73	-521.57	-519.20	-521.30
E_{*CO2}	-551.38	-550.04	-550.92	-549.67	-547.83	-544.67	-542.30	-544.41
E_{CO_2}	-0.23	-0.14	-0.15	-0.14	-0.14	-0.14	-0.14	-0.15
E_{*COOH}	-554.77	-552.72	-553.73	-552.32	-549.94	-546.68	-545.34	-548.00
E_{COOH}	-0.43	0.37	0.23	0.40	0.95	1.05	0.01	-0.54
E_{*CO}	-544.11	-542.77	-543.58	-542.38	-540.65	-537.38	-535.04	-537.05
E_{CO}	-0.85	-0.75	-0.70	-0.74	-0.84	-0.74	-0.76	-0.67
E_{*H}	-531.49	-530.14	-531.01	-529.75	-528.01	-524.75	-522.38	-524.47
E_{H}	0.15	0.25	0.24	0.26	0.17	0.27	0.27	0.28
E_{*HCOO}	-554.91	-553.28	-554.08	-552.84	-551.35	-548.23	-546.46	-549.04
E_{HCOO}	-0.56	-0.19	-0.12	-0.12	-0.46	-0.51	-1.11	-1.58

Table S10. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS), free energy (G), and Gibbs free energy change (ΔG) of critical intermediate in Mo-based

heteronuclear BACs during electrochemical CO_2RR towards C1 product and competitive HER product.

Species	E_*	E_{*CO2}	E_{ZPE}	TS	G	ΔG	E_{*COOH}	E_{ZPE}	TS	G	ΔG
Mo-Fe	-528.60	-552.32	0.32	0.14	-552.15	-0.33	-555.45	0.64	0.16	-554.98	0.36
Mo-Co	-527.34	-550.52	0.32	0.16	-550.36	0.18	-553.26	0.62	0.18	-552.81	0.75
Mo-Ir	-528.41	-551.50	0.32	0.23	-551.41	0.20	-554.37	0.62	0.17	-553.91	0.70
Mo-Rh	-527.17	-550.26	0.32	0.24	-550.18	0.19	-552.72	0.63	0.16	-552.25	1.13
Mo-Ni	-525.25	-548.32	0.30	0.19	-548.21	0.25	-550.65	0.61	0.12	-550.17	1.24
Mo-Cu	-522.24	-545.31	0.29	0.18	-545.20	0.25	-548.15	0.62	0.17	-547.69	0.70
Mo-Zn	-520.01	-543.23	0.29	0.15	-543.09	0.13	-546.62	0.63	0.17	-546.16	0.12
Mo-Ga	-521.30	-545.26	0.31	0.15	-545.10	-0.59	-548.11	0.63	0.17	-547.65	0.65
		E_{*CO}	E_{ZPE}	TS	G	ΔG	E_{*HCOO}	E_{ZPE}	TS	G	ΔG
Mo-Fe		-545.16	0.21	0.13	-545.08	-0.99	-556.41	0.61	0.15	-555.96	-0.36
Mo-Co		-543.94	0.20	0.13	-543.87	-1.94	-555.16	0.61	0.23	-554.78	-0.98
Mo-Ir		-544.98	0.21	0.13	-544.90	-1.88	-556.17	0.60	0.24	-555.80	-0.94
Mo-Rh		-543.74	0.20	0.14	-543.68	-2.32	-554.97	0.61	0.22	-554.58	-0.95
Mo-Ni		-541.96	0.32	0.14	-541.78	-2.49	-553.09	0.61	0.23	-552.71	-1.05
Mo-Cu		-538.95	0.20	0.15	-538.89	-2.09	-550.05	0.60	0.18	-549.63	-0.98
Mo-Zn		-536.67	0.21	0.13	-536.60	-1.32	-548.07	0.64	0.17	-547.60	-1.07
Mo-Ga		-537.90	0.20	0.13	-537.82	-1.06	-549.63	0.65	0.15	-549.14	-0.59
		E_{*HCOOH}	E_{ZPE}	TS	G	ΔG					
Mo-Fe		-559.17	0.93	0.24	-558.48	0.92					
Mo-Co		-557.82	0.92	0.25	-557.14	1.09					
Mo-Ir		-558.89	0.92	0.26	-558.22	1.02					
Mo-Rh		-557.70	0.92	0.24	-557.02	1.01					
Mo-Ni		-555.80	0.92	0.25	-555.13	1.03					
Mo-Cu		-552.61	0.92	0.25	-551.94	1.13					
Mo-Zn		-550.29	0.92	0.27	-549.64	1.40					
Mo-Ga		-552.49	0.93	0.28	-551.83	0.75					
		E_{*H}	E_{ZPE}	TS	G	ΔG	E_{*H2}	E_{ZPE}	TS	G	ΔG
Mo-Fe		-532.59	0.18	0.02	-532.42	-0.37	-535.35	0.29	0.17	-535.23	0.64
Mo-Co		-531.49	0.18	0.01	-531.32	-0.54	-534.09	0.31	0.18	-533.96	0.82
Mo-Ir		-532.54	0.19	0.01	-532.37	-0.52	-535.16	0.31	0.19	-535.04	0.78
Mo-Rh		-531.31	0.18	0.01	-531.14	-0.52	-533.92	0.31	0.19	-533.80	0.79
Mo-Ni		-529.44	0.18	0.01	-529.27	-0.57	-532.01	0.32	0.02	-531.71	1.01
Mo-Cu		-526.42	0.15	0.01	-526.27	-0.58	-528.99	0.37	0.11	-528.73	0.99
Mo-Zn		-524.13	0.18	0.01	-523.96	-0.51	-526.77	0.27	0.07	-526.57	0.85
Mo-Ga		-525.35	0.18	0.02	-525.18	-0.43	-528.06	0.30	0.14	-527.90	0.73

Table S11. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS),

free energy (G), and Gibbs free energy change (ΔG) of critical intermediate in Ta-based heteronuclear BACs during electrochemical CO_2RR towards C1 product and competitive HER product.

Species	E_*	E_{*CO2}	E_{ZPE}	TS	G	ΔG	E_{*COOH}	E_{ZPE}	TS	G	ΔG
Ta-Fe	-530.26	-555.00	0.31	0.16	-554.85	-1.39	-558.23	0.63	0.17	-557.77	0.28
Ta-Co	-529.04	-553.49	0.31	0.17	-553.35	-1.10	-556.09	0.61	0.19	-555.66	0.88
Ta-Ir	-530.08	-554.35	0.32	0.15	-554.17	-0.88	-556.93	0.64	0.16	-556.46	0.91
Ta-Rh	-528.89	-553.14	0.32	0.15	-552.97	-0.87	-555.51	0.63	0.16	-555.05	1.12
Ta-Ni	-527.40	-551.98	0.30	0.19	-551.86	-1.26	-553.46	0.63	0.16	-552.99	2.07
Ta-Cu	-524.33	-548.93	0.30	0.19	-548.82	-1.28	-551.29	0.62	0.17	-550.84	1.18
Ta-Zn	-522.05	-546.63	0.30	0.18	-546.51	-1.25	-549.28	0.62	0.18	-548.84	0.87
Ta-Ga	-523.37	-548.28	0.30	0.16	-548.14	-1.56	-550.89	0.63	0.18	-550.44	0.89
		E_{*CO}	E_{ZPE}	TS	G	ΔG	E_{*HCOO}	E_{ZPE}	TS	G	ΔG
Ta-Fe		-546.77	0.19	0.10	-546.69	0.19	-559.22	0.63	0.14	-558.73	-0.43
Ta-Co		-545.69	0.19	0.09	-545.59	-0.81	-558.05	0.60	0.25	-557.71	-0.91
Ta-Ir		-546.80	0.19	0.16	-546.76	-1.19	-559.02	0.61	0.23	-558.64	-1.02
Ta-Rh		-545.56	0.19	0.15	-545.52	-1.36	-557.82	0.60	0.24	-557.45	-1.04
Ta-Ni		-543.91	0.20	0.14	-543.86	-1.75	-556.39	0.61	0.24	-556.02	-0.71
Ta-Cu		-540.90	0.23	0.15	-540.82	-0.86	-553.29	0.61	0.24	-552.93	-0.66
Ta-Zn		-538.64	0.19	0.04	-538.49	-0.54	-550.93	0.63	0.18	-550.47	-0.51
Ta-Ga		-539.96	0.19	0.09	-539.86	-0.30	-552.51	0.64	0.16	-552.03	-0.45
		E_{*HCOOH}	E_{ZPE}	TS	G	ΔG					
Ta-Fe		-561.63	0.91	0.25	-560.97	1.21					
Ta-Co		-560.43	0.91	0.24	-559.76	1.40					
Ta-Ir		-561.52	0.93	0.24	-560.84	1.25					
Ta-Rh		-560.31	0.92	0.25	-559.63	1.27					
Ta-Ni		-558.65	0.90	0.25	-558.00	1.47					
Ta-Cu		-555.57	0.88	0.20	-554.89	1.49					
Ta-Zn		-553.28	0.91	0.24	-552.61	1.31					
Ta-Ga		-554.44	0.89	0.14	-553.69	1.79					
		E_{*H}	E_{ZPE}	TS	G	ΔG	E_{*H2}	E_{ZPE}	TS	G	ΔG
Ta-Fe		-534.89	0.18	0.02	-534.73	-1.03	-537.11	0.29	0.11	-536.93	1.25
Ta-Co		-533.68	0.18	0.02	-533.52	-1.03	-535.79	0.32	0.15	-535.63	1.34
Ta-Ir		-534.66	0.18	0.01	-534.49	-0.96	-536.84	0.30	0.14	-536.69	1.25
Ta-Rh		-533.44	0.18	0.01	-533.28	-0.94	-535.65	0.31	0.14	-535.48	1.25
Ta-Ni		-532.06	0.18	0.02	-531.90	-1.05	-534.15	0.32	0.16	-533.99	1.35
Ta-Cu		-528.98	0.18	0.01	-528.81	-1.03	-531.08	0.33	0.16	-530.92	1.34
Ta-Zn		-526.66	0.18	0.02	-526.50	-1.00	-528.80	0.31	0.17	-528.66	1.29
Ta-Ga		-527.93	0.18	0.02	-527.77	-0.95	-530.12	0.30	0.19	-530.01	1.21

Table S12. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS), free energy (G), and Gibbs free energy change (ΔG) of critical intermediate in V-based heteronuclear BACs during electrochemical CO_2RR towards C1 product and competitive HER product.

Species	E_*	E_{*CO2}	E_{ZPE}	TS	G	ΔG	E_{*COOH}	E_{ZPE}	TS	G	ΔG
V-Fe	-528.40	-552.25	0.32	0.15	-552.08	-0.48	-555.76	0.64	0.15	-555.27	0.01
V-Co	-527.11	-550.86	0.32	0.11	-550.65	-0.34	-553.71	0.63	0.16	-553.24	0.61
V-Ir	-528.09	-551.78	0.33	0.16	-551.62	-0.32	-554.64	0.64	0.16	-554.15	0.66
V-Rh	-526.82	-550.48	0.33	0.15	-550.31	-0.28	-553.21	0.64	0.16	-552.73	0.78
V-Ni	-525.46	-548.54	0.32	0.23	-548.44	0.22	-551.20	0.57	0.22	-550.84	0.80
V-Cu	-522.25	-545.31	0.33	0.22	-545.21	0.25	-548.14	0.62	0.18	-547.70	0.70
V-Zn	-519.85	-542.94	0.28	0.17	-542.83	0.23	-546.57	0.62	0.18	-546.12	-0.09
V-Ga	-521.41	-545.31	0.31	0.15	-545.15	-0.53	-548.51	0.63	0.18	-548.06	0.29
		E_{*CO}	E_{ZPE}	TS	G	ΔG	E_{*HCOO}	E_{ZPE}	TS	G	ΔG
V-Fe		-544.52	0.20	0.14	-544.47	-0.09	-556.45	0.61	0.14	-555.98	-0.45
V-Co		-543.47	0.20	0.10	-543.38	-1.02	-554.82	0.62	0.19	-554.38	-0.28
V-Ir		-544.46	0.20	0.16	-544.42	-1.16	-555.78	0.61	0.22	-555.39	-0.33
V-Rh		-543.16	0.20	0.16	-543.12	-1.28	-554.54	0.60	0.24	-554.17	-0.41
V-Ni		-541.62	0.20	0.15	-541.57	-1.61	-553.24	0.61	0.22	-552.85	-0.96
V-Cu		-538.45	0.22	0.10	-538.33	-1.52	-550.06	0.61	0.22	-549.67	-1.02
V-Zn		-536.07	0.20	0.10	-535.97	-0.74	-548.03	0.63	0.19	-547.60	-1.32
V-Ga		-537.60	0.20	0.09	-537.50	-0.32	-550.04	0.64	0.17	-549.57	-0.97
		E_{*HCOOH}	E_{ZPE}	TS	G	ΔG					
V-Fe		-559.18	0.94	0.25	-558.50	0.93					
V-Co		-558.04	0.94	0.24	-557.34	0.49					
V-Ir		-559.07	0.94	0.23	-558.36	0.49					
V-Rh		-557.78	0.94	0.23	-557.07	0.55					
V-Ni		-556.01	0.93	0.25	-555.33	0.97					
V-Cu		-552.78	0.92	0.20	-552.06	1.06					
V-Zn		-550.40	0.92	0.20	-549.68	1.37					
V-Ga		-551.85	0.92	0.20	-551.13	1.89					
		E_{*H}	E_{ZPE}	TS	G	ΔG	E_{*H2}	E_{ZPE}	TS	G	ΔG
V-Fe		-532.00	0.17	0.02	-531.84	0.00	-535.15	0.30	0.21	-535.05	0.24
V-Co		-530.78	0.18	0.02	-530.62	-0.06	-533.86	0.31	0.19	-533.74	0.33
V-Ir		-531.70	0.18	0.02	-531.54	-0.01	-534.85	0.32	0.15	-534.67	0.32
V-Rh		-530.43	0.17	0.02	-530.27	0.00	-533.58	0.32	0.16	-533.43	0.30
V-Ni		-529.17	0.18	0.01	-529.00	-0.10	-532.21	0.29	0.11	-532.03	0.42
V-Cu		-525.94	0.17	0.01	-525.78	-0.08	-528.98	0.28	0.09	-528.79	0.43
V-Zn		-523.52	0.17	0.02	-523.36	-0.07	-526.60	0.30	0.10	-526.40	0.41
V-Ga		-525.08	0.17	0.02	-524.92	-0.06	-528.17	0.30	0.13	-528.00	0.37

Table S13. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS), free energy (G), and Gibbs free energy change (ΔG) of critical intermediate in Ti-based heteronuclear BACs during electrochemical CO_2RR towards C1 product and competitive HER product.

Species	E_*	E_{*CO2}	E_{ZPE}	TS	G	ΔG	E_{*COOH}	E_{ZPE}	TS	G	ΔG
Ti-Fe	-527.65	-551.90	0.32	0.16	-551.74	-0.89	-555.39	0.64	0.16	-554.91	0.03
Ti-Co	-526.44	-550.64	0.32	0.17	-550.49	-0.85	-553.70	0.64	0.16	-553.23	0.46
Ti-Ir	-527.47	-551.55	0.33	0.15	-551.38	-0.69	-554.67	0.64	0.16	-554.18	0.40
Ti-Rh	-526.20	-550.25	0.32	0.17	-550.10	-0.69	-553.22	0.64	0.16	-552.74	0.56
Ti-Ni	-524.82	-548.30	0.29	0.23	-548.24	-0.21	-551.01	0.59	0.21	-550.63	0.81
Ti-Cu	-521.65	-545.17	0.32	0.09	-544.95	-0.09	-548.03	0.60	0.21	-547.65	0.50
Ti-Zn	-519.31	-542.83	0.29	0.23	-542.77	-0.25	-546.29	0.62	0.17	-545.84	0.13
Ti-Ga	-520.88	-545.19	0.30	0.16	-545.05	-0.96	-548.53	0.63	0.18	-548.08	0.16
		E_{*CO}	E_{ZPE}	TS	G	ΔG	E_{*HCOO}	E_{ZPE}	TS	G	ΔG
Ti-Fe		-543.54	0.18	0.17	-543.53	0.50	-555.81	0.63	0.17	-555.35	-0.16
Ti-Co		-542.36	0.19	0.18	-542.35	-0.01	-554.66	0.62	0.21	-554.26	-0.32
Ti-Ir		-543.35	0.19	0.16	-543.33	-0.03	-555.62	0.60	0.25	-555.27	-0.44
Ti-Rh		-542.09	0.19	0.16	-542.06	-0.21	-554.34	0.60	0.25	-553.98	-0.43
Ti-Ni		-540.83	0.19	0.16	-540.80	-1.06	-553.13	0.61	0.24	-552.77	-1.09
Ti-Cu		-537.65	0.19	0.17	-537.64	-0.88	-549.94	0.60	0.18	-549.52	-1.13
Ti-Zn		-535.32	0.18	0.18	-535.31	-0.36	-547.61	0.63	0.18	-547.16	-0.95
Ti-Ga		-537.04	0.19	0.16	-537.02	0.18	-549.46	0.64	0.16	-548.98	-0.48
		E_{*HCOOH}	E_{ZPE}	TS	G	ΔG					
Ti-Fe		-558.71	0.93	0.29	-558.07	0.73					
Ti-Co		-557.55	0.93	0.27	-556.89	0.82					
Ti-Ir		-558.60	0.93	0.25	-557.92	0.79					
Ti-Rh		-557.33	0.93	0.26	-556.65	0.78					
Ti-Ni		-555.95	0.93	0.25	-555.27	0.95					
Ti-Cu		-552.79	0.93	0.24	-552.10	0.87					
Ti-Zn		-550.44	0.93	0.25	-549.76	0.85					
Ti-Ga		-552.07	0.91	0.18	-551.34	1.09					
		E_{*H}	E_{ZPE}	TS	G	ΔG	E_{*H2}	E_{ZPE}	TS	G	ΔG
Ti-Fe		-531.15	0.15	0.02	-531.02	0.07	-534.40	0.29	0.11	-534.22	0.25
Ti-Co		-529.99	0.15	0.02	-529.86	0.03	-533.19	0.31	0.13	-533.01	0.29
Ti-Ir		-530.94	0.15	0.02	-530.81	0.11	-534.23	0.32	0.17	-534.09	0.17
Ti-Rh		-529.61	0.15	0.02	-529.48	0.17	-532.96	0.32	0.17	-532.82	0.11
Ti-Ni		-528.56	0.16	0.02	-528.43	-0.16	-531.58	0.31	0.14	-531.41	0.46
Ti-Cu		-525.37	0.15	0.02	-525.24	-0.14	-528.40	0.31	0.14	-528.23	0.46

Ti-Zn		-523.02	0.15	0.02	-522.89	-0.14	-526.06	0.30	0.16	-525.92	0.41
Ti-Ga		-524.91	0.15	0.02	-524.78	-0.46	-527.64	0.31	0.20	-527.53	0.70

Table S14. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS), free energy (G), and Gibbs free energy change (ΔG) of critical intermediate in Cr-based heteronuclear BACs during electrochemical CO_2RR towards C1 product and competitive HER product.

Species	E_*	E_{*CO2}	E_{ZPE}	TS	G	ΔG	E_{*COOH}	E_{ZPE}	TS	G	ΔG
Cr-Fe	-528.49	-551.91	0.32	0.15	-551.73	-0.03	-555.26	0.64	0.15	-554.77	0.16
Cr-Co	-527.53	-550.63	0.32	0.25	-550.56	0.18	-553.45	0.64	0.16	-552.97	0.78
Cr-Ir	-528.42	-551.54	0.32	0.24	-551.46	0.17	-554.57	0.63	0.22	-554.16	0.50
Cr-Rh	-527.15	-550.26	0.32	0.23	-550.17	0.19	-553.11	0.63	0.21	-552.70	0.67
Cr-Ni	-525.56	-548.65	0.32	0.25	-548.58	0.19	-550.63	0.57	0.23	-550.29	1.49
Cr-Cu	-522.30	-545.38	0.32	0.22	-545.28	0.23	-547.75	0.62	0.17	-547.30	1.17
Cr-Zn	-519.81	-542.89	0.31	0.19	-542.77	0.25	-546.09	0.63	0.17	-545.63	0.34
Cr-Ga	-521.52	-544.65	0.32	0.15	-544.49	0.24	-548.38	0.60	0.20	-547.98	-0.29
		E_{*CO}	E_{ZPE}	TS	G	ΔG	E_{*HCOO}	E_{ZPE}	TS	G	ΔG
Cr-Fe		-544.63	0.21	0.12	-544.54	-0.65	-555.99	0.62	0.19	-555.55	-0.37
Cr-Co		-543.49	0.35	0.23	-543.37	-1.28	-554.40	0.61	0.15	-553.94	0.06
Cr-Ir		-544.41	0.19	0.10	-544.32	-1.05	-555.23	0.60	0.17	-554.80	0.10
Cr-Rh		-543.12	0.14	0.23	-543.21	-1.40	-553.98	0.61	0.22	-553.59	0.03
Cr-Ni		-541.52	0.14	0.18	-541.57	-2.17	-552.52	0.61	0.21	-552.12	-0.09
Cr-Cu		-538.29	0.15	0.19	-538.33	-1.91	-549.32	0.63	0.16	-548.84	-0.11
Cr-Zn		-535.88	0.15	0.22	-535.96	-1.22	-547.44	0.64	0.17	-546.97	-0.76
Cr-Ga		-537.47	0.15	0.18	-537.49	-0.40	-549.59	0.64	0.16	-549.11	-1.18
		E_{*HCOOH}	E_{ZPE}	TS	G	ΔG					
Cr-Fe		-558.75	0.94	0.22	-558.03	0.97					
Cr-Co		-557.62	0.91	0.27	-556.97	0.42					
Cr-Ir		-558.55	0.91	0.26	-557.90	0.35					
Cr-Rh		-557.27	0.91	0.27	-556.62	0.41					
Cr-Ni		-555.62	0.91	0.20	-554.91	0.66					
Cr-Cu		-552.40	0.90	0.22	-551.72	0.57					
Cr-Zn		-549.98	0.91	0.20	-549.28	1.14					
Cr-Ga		-551.81	0.91	0.10	-551.01	1.55					
		E_{*H}	E_{ZPE}	TS	G	ΔG	E_{*H2}	E_{ZPE}	TS	G	ΔG
Cr-Fe		-532.04	0.19	0.01	-531.87	0.07	-535.37	0.30	0.16	-535.23	0.08
Cr-Co		-530.88	0.20	0.01	-530.69	0.29	-534.28	0.30	0.14	-534.11	0.03
Cr-Ir		-531.81	0.19	0.01	-531.63	0.24	-535.18	0.32	0.17	-535.03	0.05
Cr-Rh		-530.53	0.19	0.01	-530.35	0.25	-533.91	0.32	0.17	-533.76	0.03

Cr-Ni		-528.89	0.20	0.01	-528.71	0.30	-532.30	0.28	0.10	-532.13	0.03
Cr-Cu		-525.65	0.19	0.01	-525.47	0.28	-529.05	0.28	0.09	-528.86	0.06
Cr-Zn		-523.21	0.19	0.01	-523.03	0.23	-526.49	0.32	0.10	-526.27	0.20
Cr-Ga		-524.66	0.19	0.01	-524.48	0.49	-528.27	0.29	0.12	-528.11	-0.18

Table S15. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS), free energy (G), and Gibbs free energy change (ΔG) of critical intermediate in Mn-based heteronuclear BACs during electrochemical CO_2RR towards C1 product and competitive HER product.

Species	E_*	E_{*CO2}	E_{ZPE}	TS	G	ΔG	E_{*COOH}	E_{ZPE}	TS	G	ΔG
Mn-Fe	-528.19	-551.38	0.39	0.15	-551.14	0.26	-554.77	0.61	0.16	-554.33	0.01
Mn-Co	-526.94	-550.04	0.32	0.24	-549.96	0.19	-552.72	0.62	0.17	-552.27	0.88
Mn-Ir	-527.81	-550.92	0.32	0.24	-550.83	0.18	-553.73	0.63	0.16	-553.26	0.77
Mn-Rh	-526.56	-549.67	0.32	0.23	-549.58	0.19	-552.32	0.62	0.17	-551.87	0.91
Mn-Ni	-524.73	-547.83	0.32	0.24	-547.76	0.18	-549.94	0.59	0.18	-549.54	1.41
Mn-Cu	-521.57	-544.67	0.32	0.23	-544.58	0.20	-546.68	0.58	0.20	-546.30	1.48
Mn-Zn	-519.20	-542.30	0.31	0.19	-542.17	0.23	-545.34	0.60	0.19	-544.93	0.44
Mn-Ga	-521.30	-544.41	0.32	0.24	-544.34	0.17	-548.00	0.61	0.19	-547.58	-0.04
		E_{*CO}	E_{ZPE}	TS	G	ΔG	E_{*HCOO}	E_{ZPE}	TS	G	ΔG
Mn-Fe		-544.11	0.29	0.07	-543.90	-0.46	-554.54	0.60	0.17	-554.11	0.48
Mn-Co		-542.77	0.22	0.13	-542.68	-1.29	-553.17	0.61	0.17	-552.72	0.68
Mn-Ir		-543.58	0.21	0.09	-543.46	-1.09	-554.01	0.61	0.22	-553.62	0.66
Mn-Rh		-542.38	0.22	0.14	-542.30	-1.32	-552.78	0.61	0.22	-552.40	0.63
Mn-Ni		-540.65	0.21	0.08	-540.51	-1.86	-551.21	0.61	0.22	-550.82	0.38
Mn-Cu		-537.38	0.23	0.07	-537.23	-1.82	-547.96	0.61	0.14	-547.49	0.54
Mn-Zn		-535.04	0.20	0.03	-534.87	-0.82	-545.71	0.63	0.18	-545.26	0.36
Mn-Ga		-537.05	0.23	0.08	-536.90	-0.21	-547.88	0.63	0.18	-547.43	0.36
		E_{*HCOOH}	E_{ZPE}	TS	G	ΔG					
Mn-Fe		-558.42	0.91	0.26	-557.77	-0.21					
Mn-Co		-557.07	0.91	0.28	-556.44	-0.27					
Mn-Ir		-557.95	0.91	0.27	-557.32	-0.25					
Mn-Rh		-556.73	0.91	0.26	-556.07	-0.23					
Mn-Ni		-554.86	0.91	0.22	-554.17	0.10					
Mn-Cu		-551.74	0.94	0.23	-551.04	-0.10					
Mn-Zn		-549.42	0.91	0.27	-548.77	-0.07					
Mn-Ga		-551.49	0.92	0.18	-550.76	0.12					
		E_{*H}	E_{ZPE}	TS	G	ΔG	E_{*H2}	E_{ZPE}	TS	G	ΔG
Mn-Fe		-531.49	0.20	0.01	-531.29	0.34	-535.03	0.32	0.17	-534.89	-0.15
Mn-Co		-530.14	0.20	0.01	-529.94	0.44	-533.68	0.29	0.05	-533.45	-0.06

Mn-Ir	-531.01	0.20	0.01	-530.81	0.44	-534.56	0.29	0.05	-534.31	-0.05
Mn-Rh	-529.75	0.20	0.01	-529.56	0.45	-533.32	0.29	0.11	-533.14	-0.13
Mn-Ni	-528.01	0.20	0.01	-527.82	0.36	-531.49	0.30	0.04	-531.24	0.03
Mn-Cu	-524.75	0.20	0.01	-524.55	0.46	-528.19	0.35	0.05	-527.89	0.12
Mn-Zn	-522.38	0.13	0.01	-522.25	0.39	-525.96	0.29	0.13	-525.80	-0.09
Mn-Ga	-524.47	0.19	0.01	-524.29	0.46	-528.05	0.29	0.12	-527.89	-0.15

Table S16. The detailed electronic energy (E_*), zero-point energy (E_{ZPE}), entropy corrections (TS), and free energy (G) of isolated molecule during electrochemical CO_2RR towards C1 product and competitive HER product.

Species	E_*	E_{ZPE}	TS	G
CO_2	-22.96	0.31	0.66	-23.21
CO	-14.84	0.14	0.61	-15.31
H_2O	-14.25	0.59	0.58	-14.24
H_2	-6.76	0.27	0.40	-6.89
HCOOH	-29.97	0.90	0.99	-30.06

In this work, we consider two coordination forms of BACs, i.e., 3-coordinated and 4-coordinated metal-anchored N-doped graphene, as shown in Fig. S1. We select three metals, Fe, Mn, and Mo, as the representative to compare the DFT energy of the different coordination forms. Due to the significantly lower energy of 4-coordinated form, thus all of our subsequent investigation are based on the 4-coordinated form of BACs.

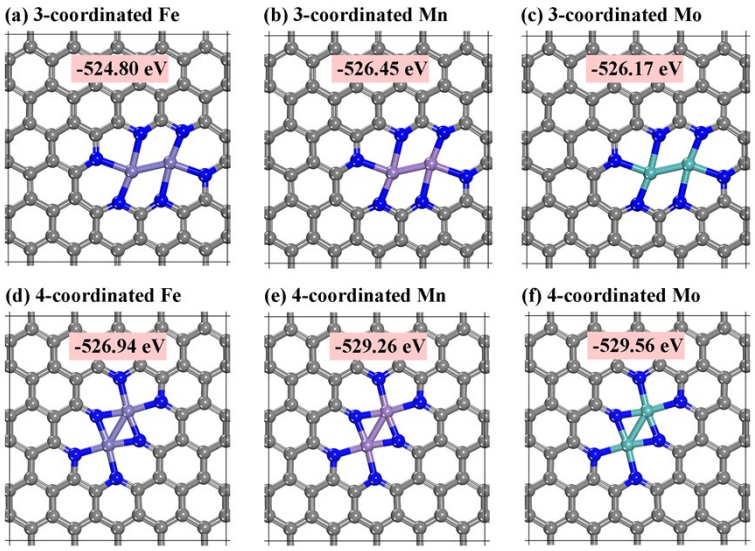

Fig. S1 The most stable structures and the DFT energy of 3-coordinated and 4-coordinated metal-anchored N-doped graphene homonuclear BACs.

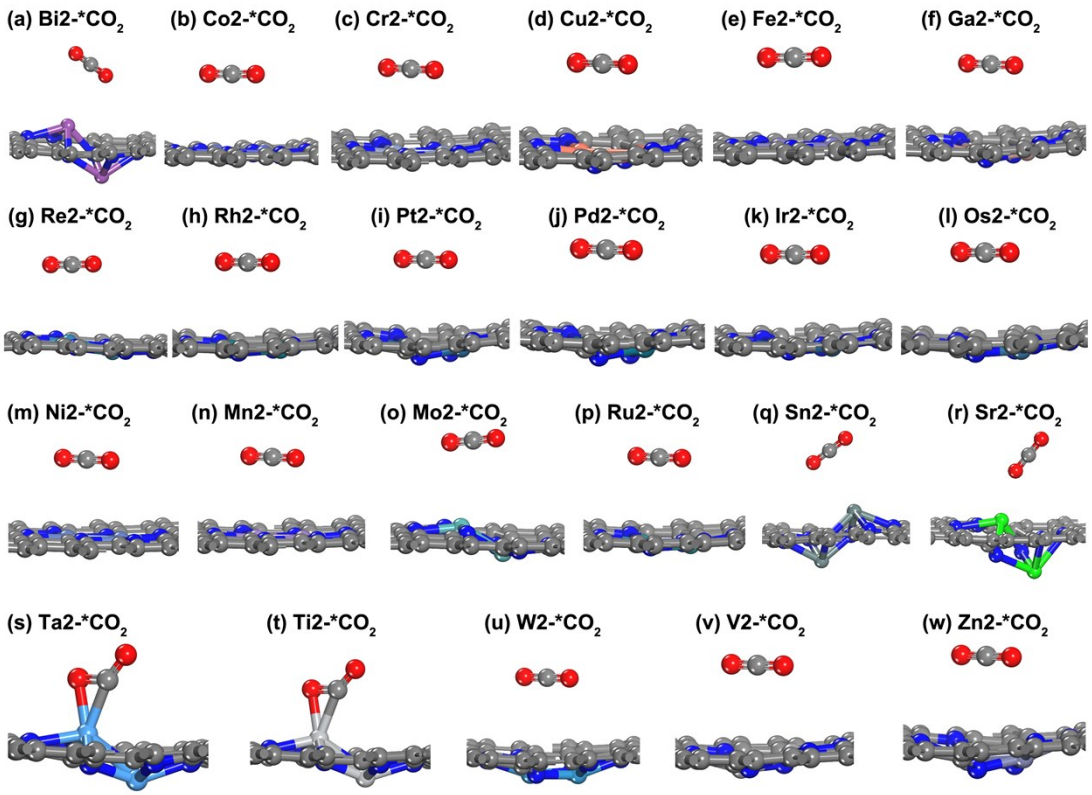

Fig. S2 The most stable structures of $*CO_2$ adsorbed on 23 kinds of homonuclear BACs.

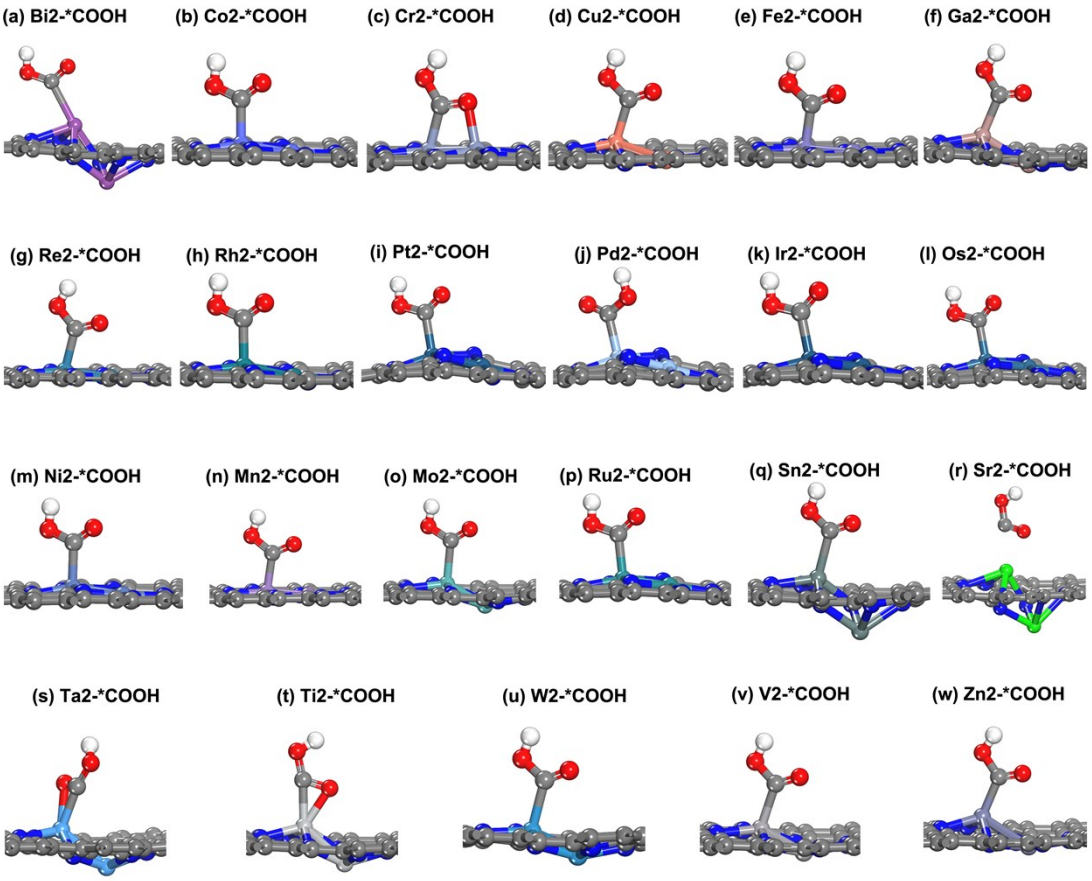

Fig. S3 The most stable structures of *COOH adsorbed on 23 kinds of homonuclear BACs.

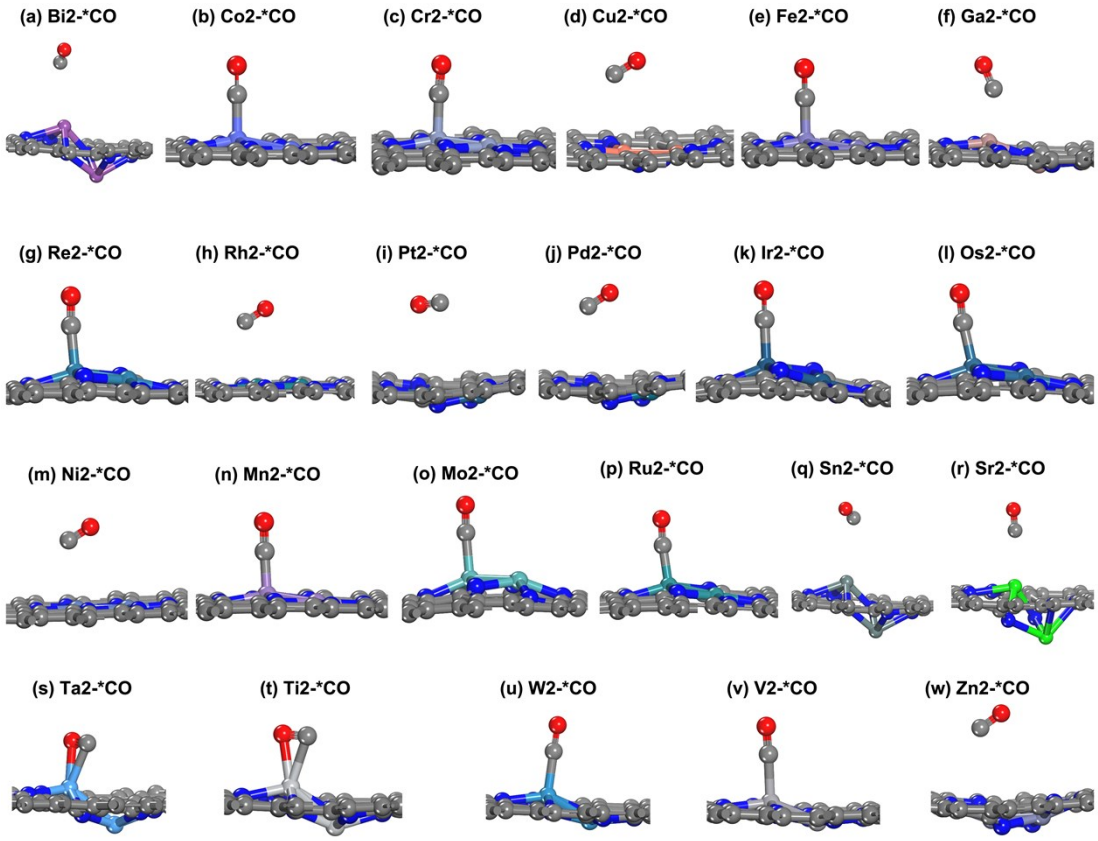

Fig. S4 The most stable structures of *CO adsorbed on 23 kinds of homonuclear BACs.

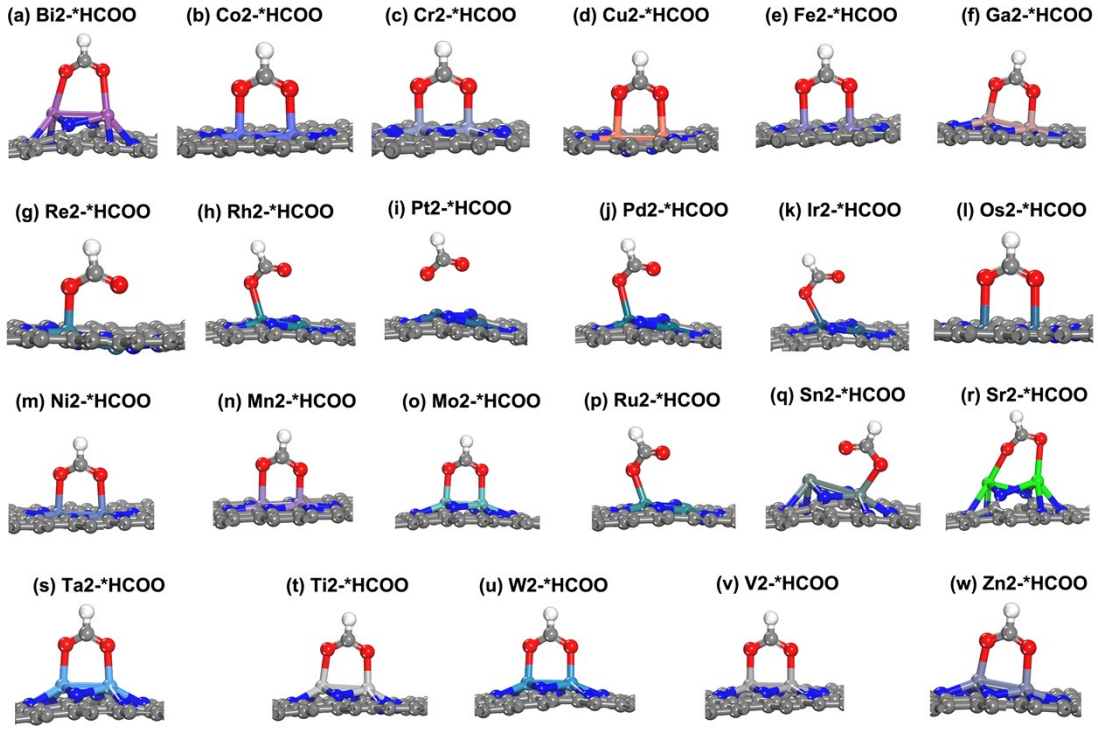

Fig. S5 The most stable structures of *HCOO adsorbed on 23 kinds of homonuclear

BACs.

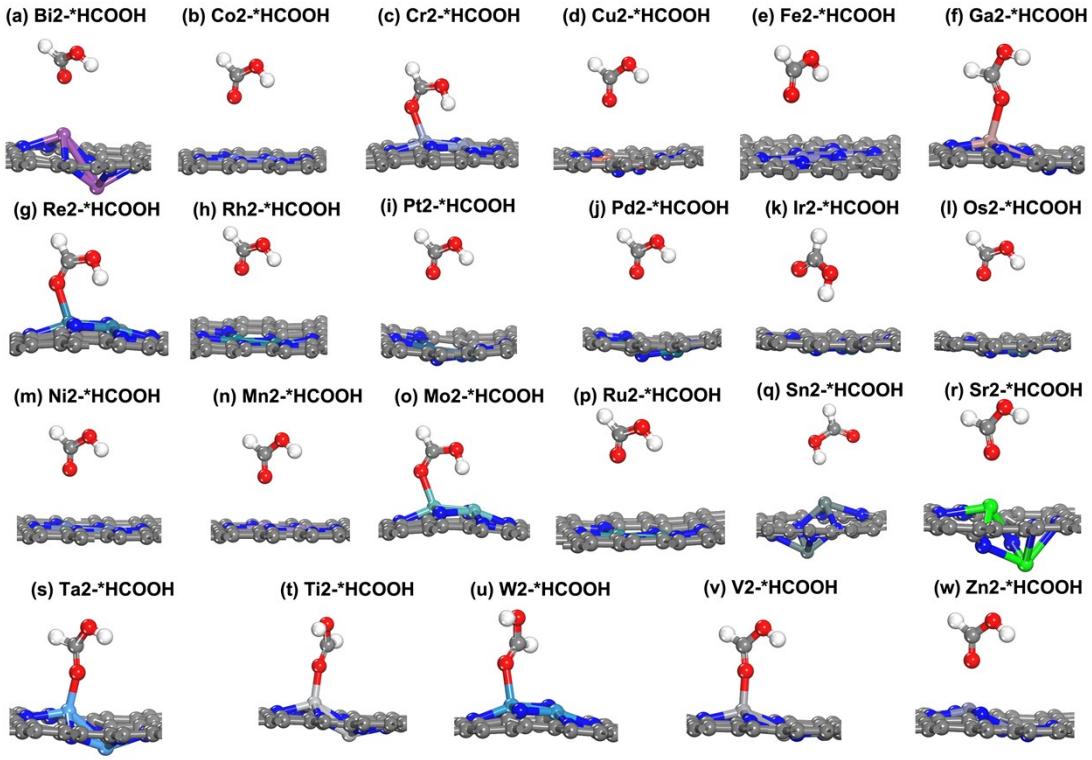

Fig. S6 The most stable structures of *HCOOH adsorbed on 23 kinds of homonuclear

BACs.

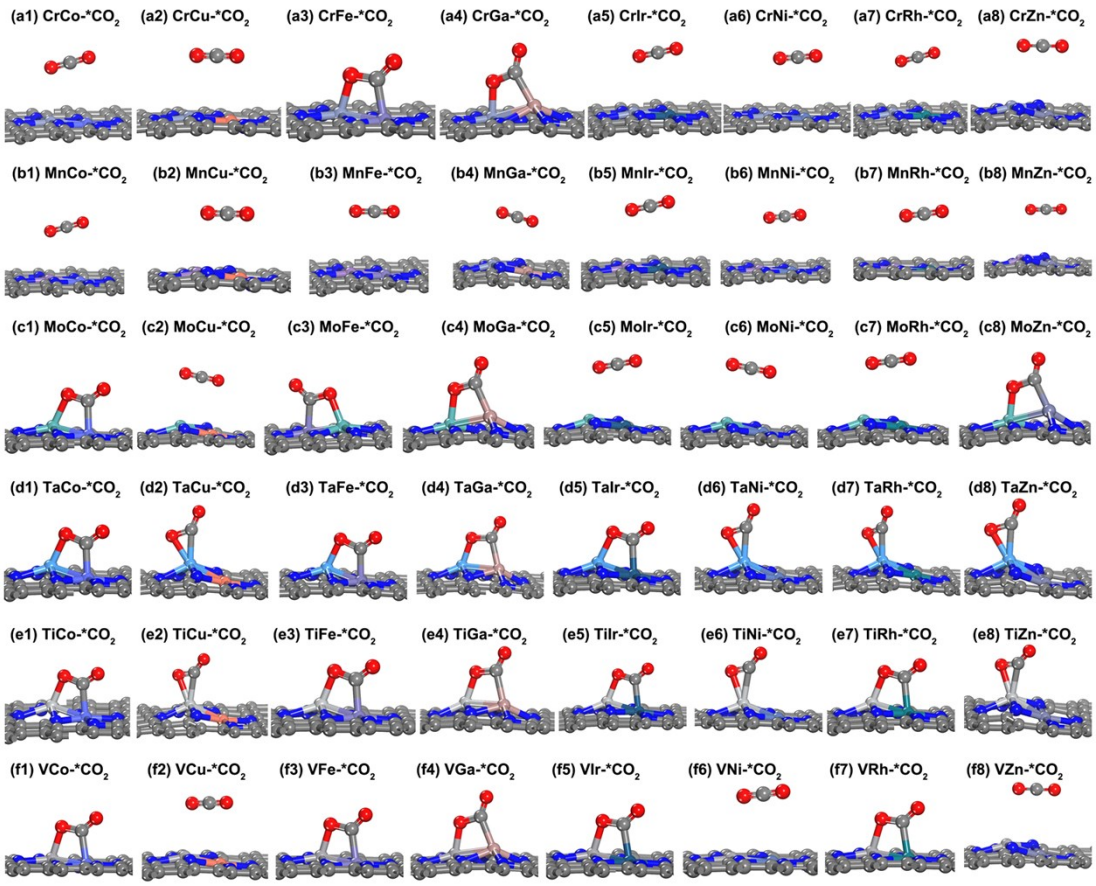

Fig. S7 The most stable structures of $*CO_2$ adsorbed on 48 kinds of heteronuclear BACs.

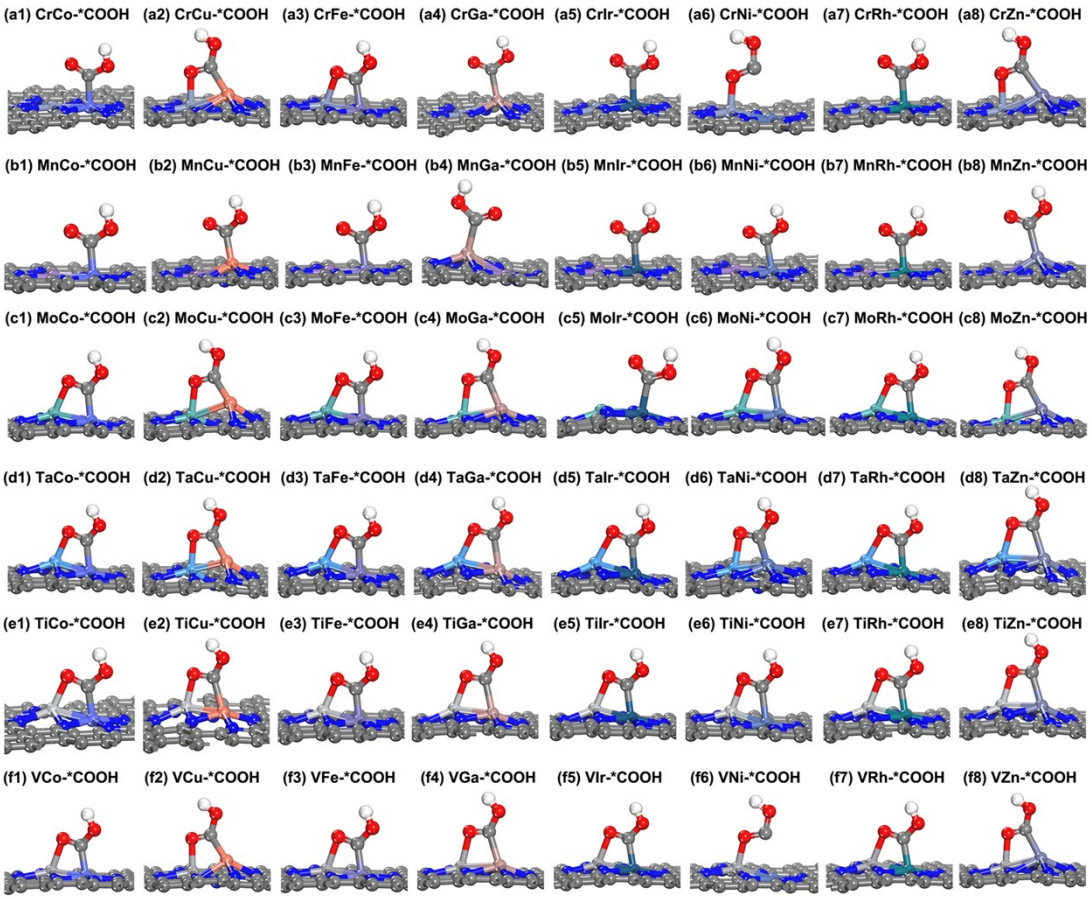

Fig. S8 The most stable structures of *COOH adsorbed on 48 kinds of heteronuclear BACs.

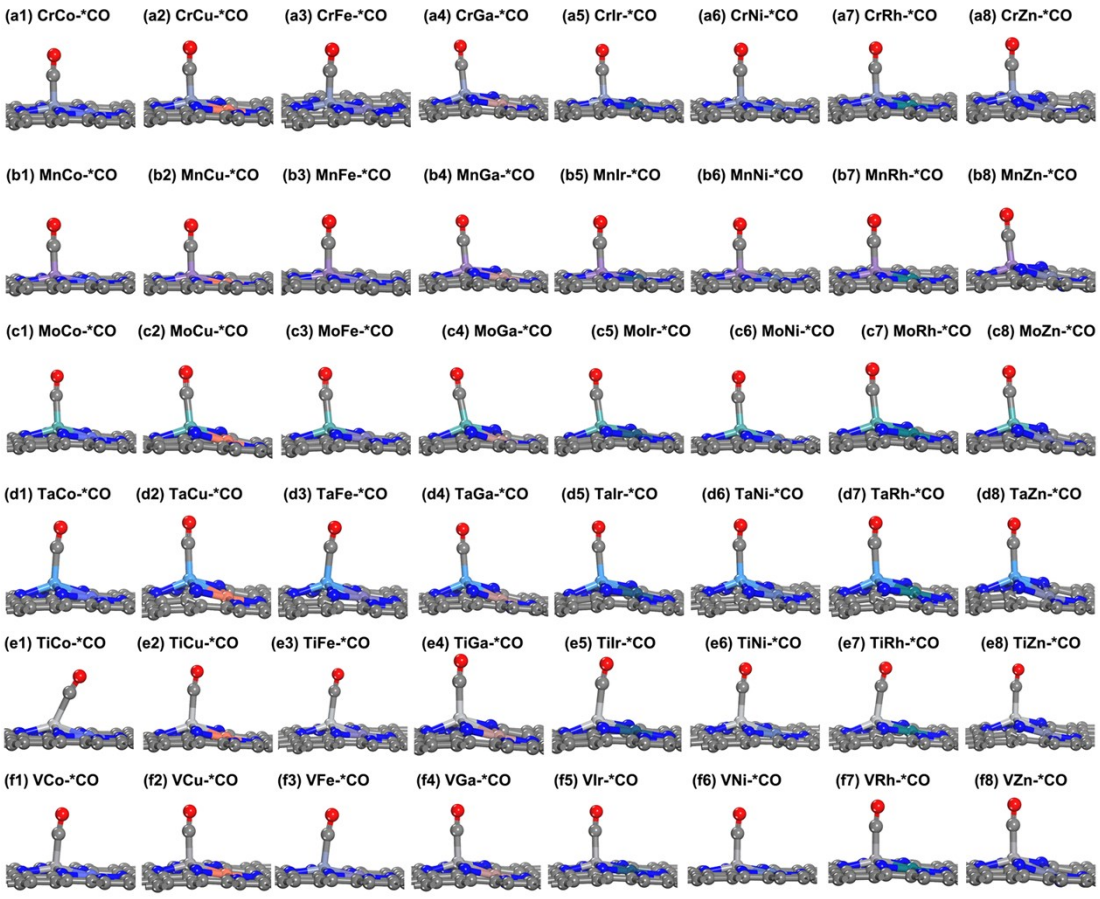

Fig. S9 The most stable structures of *CO adsorbed on 48 kinds of heteronuclear BACs.

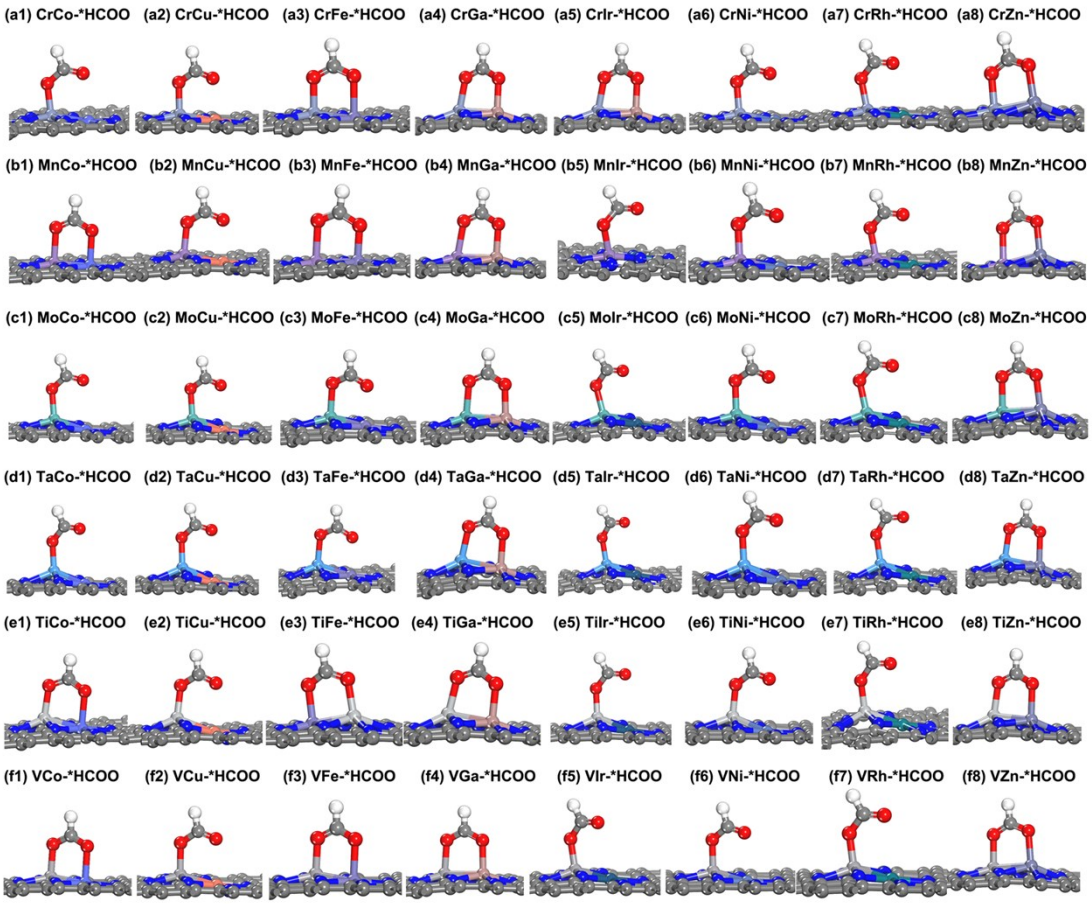

Fig. S10 The most stable structures of *HCOO adsorbed on 48 kinds of heteronuclear BACs.

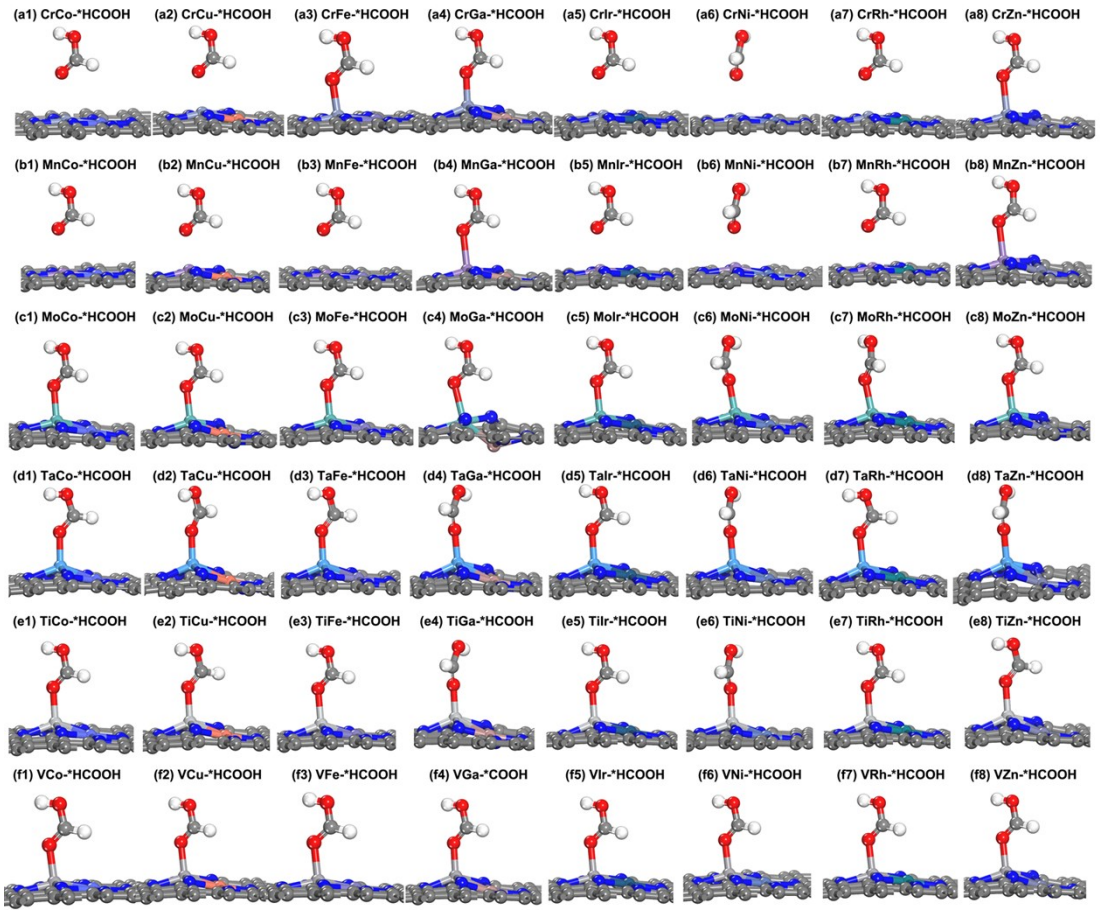

Fig. S11 The most stable structures of *HCOOH adsorbed on 48 kinds of heteronuclear BACs.

REFERENCES

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