Supporting Information for

Design of Bimetallic Atomic Catalysts for CO_2 Reduction Based on an Effective Descriptor

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Competition of COOH and HCOO formation in gas phase

We first study the adsorption properties of the intermediates of CO_2 reduction on BACs. For X atoms have strong interaction with O atom (from the IIIB group to the VIB group), the corresponding BACs prefer to form *HCOO in bidentate adsorption configuration (the two O atoms bind to M and X respectively), while for X have moderate or weak interaction with O atom (from the VIIB group to the IIB group), the BACs adsorb *COOH and *HCOO with onefold configuration with C (O) atom binding to M site.[1] These properties prove the adsorption properties of TMs in SACs (M-N_4-Gra) can be used for designing BACs (MX-N_6-Gra), thus the MX-N_6-Gras with X from the VIIB group to the IIB group show selectivity to COOH rather than HCOO, which are potentially active for CO production.

Comparison between our descriptor and other descriptors

To justify the performance of our descriptor, we fit the adsorption energy of *CO, *COOH, and *HCOO of BACs with other type descriptors, such as φ,[2] S_d (the number of *d*-electrons of transition-metal element), S_v (the number of *d*- and *s*-electrons of transition-metal element) and χ (the electronegativity of transition-metal element), see Figure S3~S6. We find that our descriptor ψ has better performance than the other descriptors in correlating with the adsorption energy of BACs with bigger R^2.

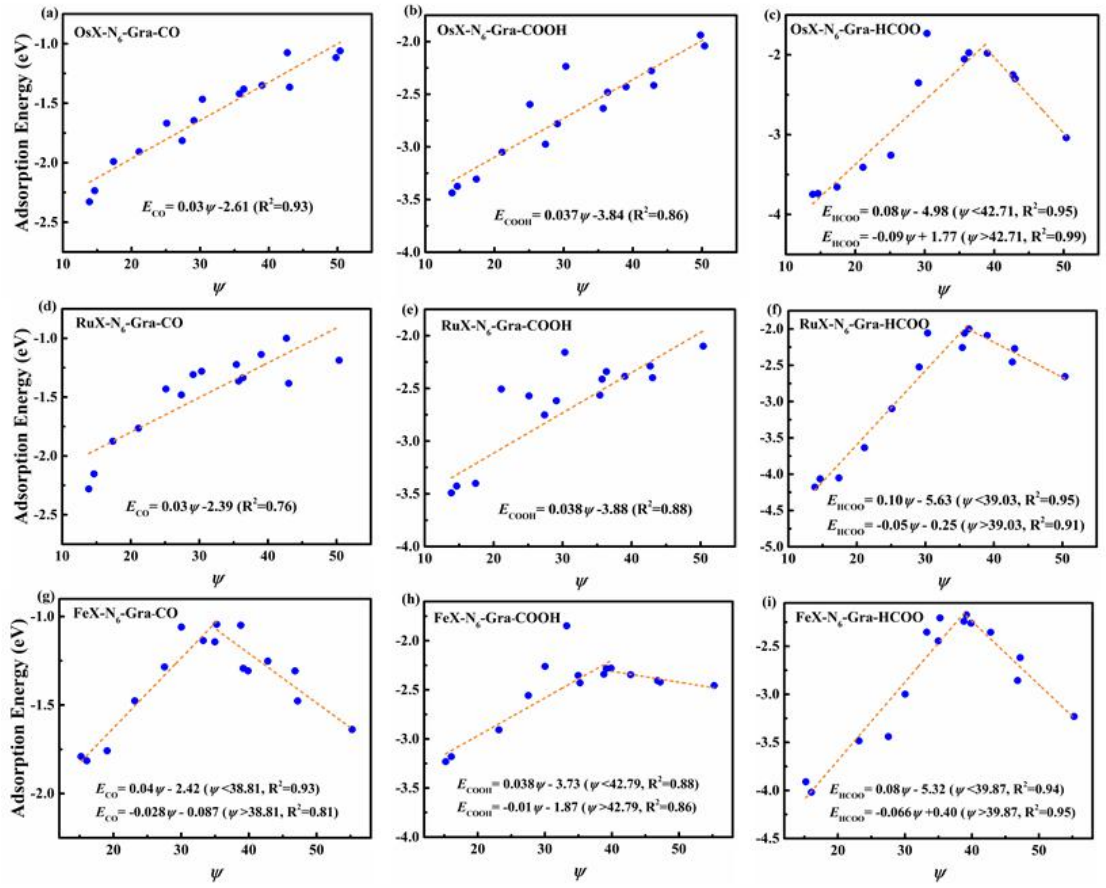

Figure S1. Adsorption energy of *CO, *COOH and *HCOO on MX-N_6-Gra (M=Os, Ru, Fe) versus ψ_1.

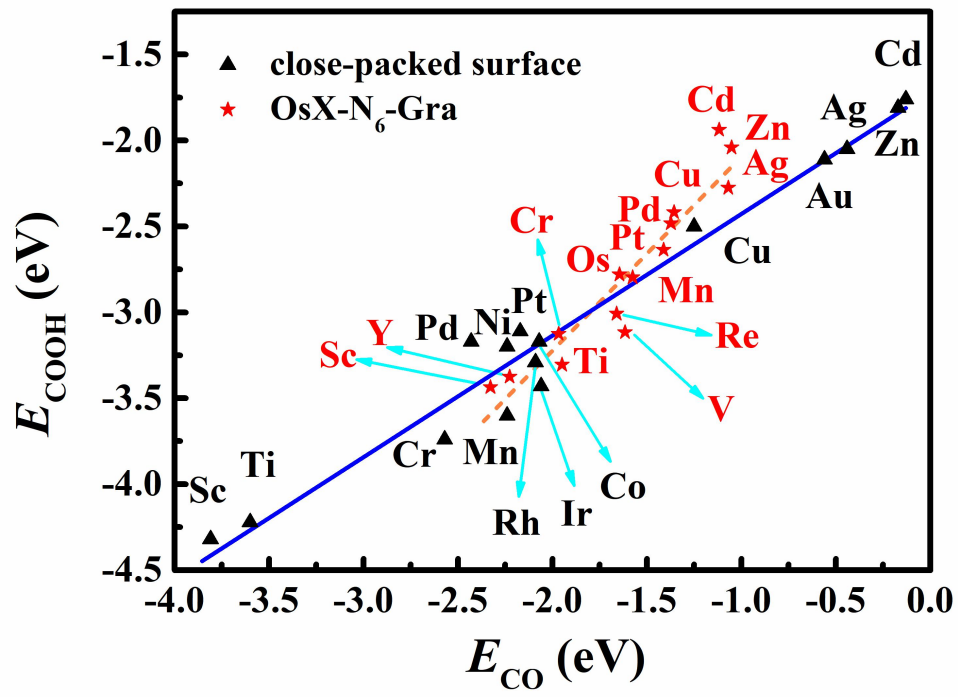

Figure S2. Correlation between E_{CO} and E_{COOH} for both OsX-N_6-Gra (red pentagram) and close-packed surfaces [3] (black triangle). The slope of E_{CO} versus E_{COOH} on OsX-N_6-Gra is bigger than that on close-packed surfaces.

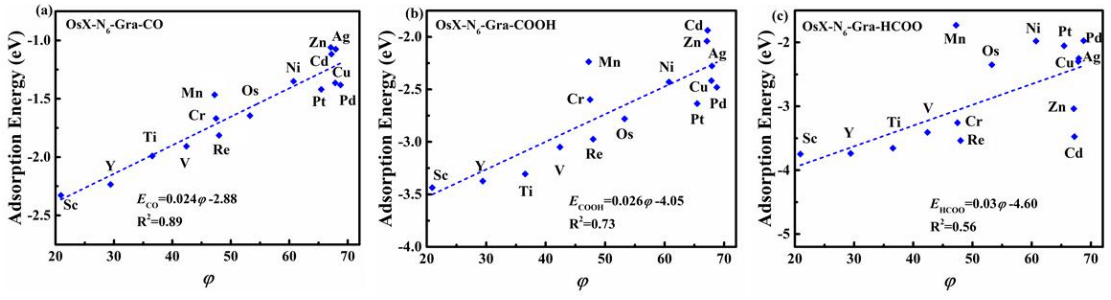

Figure S3. Adsorption energy of *CO, *COOH and *HCOO on OsX-N_6-Gra with respect to descriptor φ in (a), (b) and (c) respectively, [2] $\varphi = \sqrt{S_{d_1} S_{d_2}} \frac{\chi_{M_1} + \chi_{M_2} + n_N \chi_N}{\chi_{C/O}}$. (where S_{d1} and S_{d2} represent the number of *d*-electrons of each TM atom respectively, $\chi_{M1}$and χ_{M2} represent the electronegativity of each TM atom respectively, n_N represent the number of the nitrogen atoms in the active site, χ_N represent the electronegativity of nitrogen atom, $\chi_{C/O}$ represents the electronegativity of the terminal atom of adsorbate).

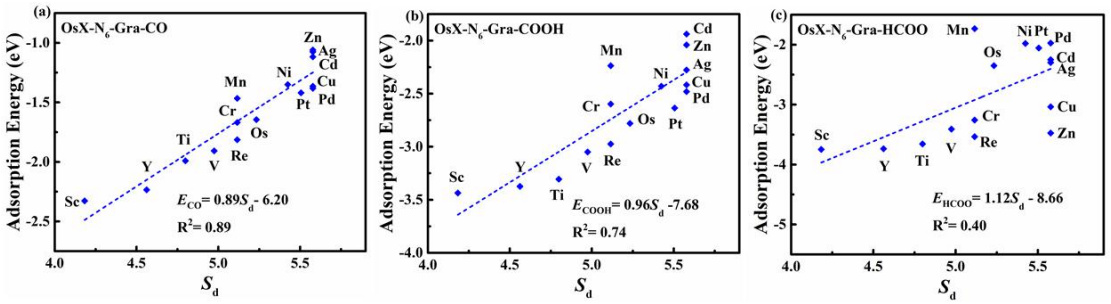

Figure S4. Adsorption energy of *CO, *COOH and *HCOO on OsX-N_6-Gra with respect to descriptor S_d (S_d is the number of *d*-electrons of transition-metal element) in (a), (b) and (c) respectively.

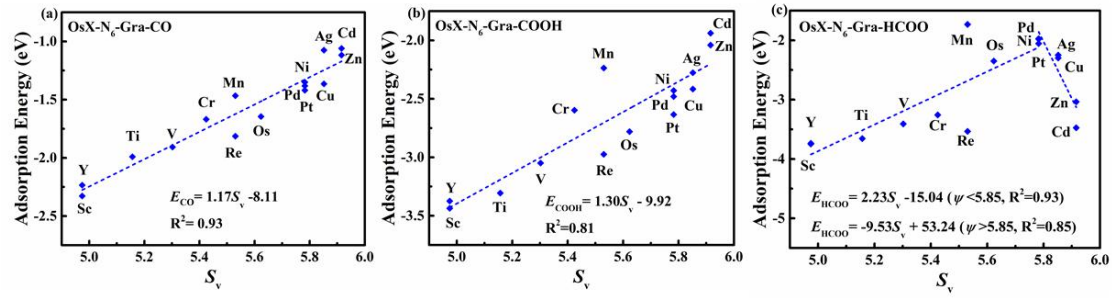

Figure S5. Adsorption energy of *CO, *COOH and *HCOO on OsX-N_6-Gra with respect to descriptor S_v (S_v is the valence-electron number of transition-metal element) in (a), (b) and (c) respectively.

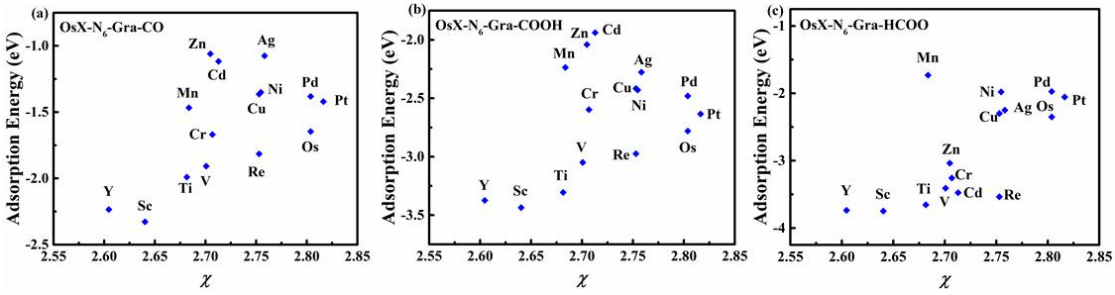

Figure S6. Adsorption energy of *CO, *COOH and *HCOO on OsX-N_6-Gra with respect to descriptor χ (χ is the electronegativity of transition metal element) in (a), (b) and (c) respectively.

Table S1 The value of U^0 of each step in $CO_2 \rightarrow CO$.[4]

Step	U^0
$CO_2 \rightarrow$*COOH	-0.11
*COOH→*CO	-0.08

Table S2 The adsorption energy of *CO and *HCOO on SACs.[5]

M-N_4-Gra	E_{CO}	M-N_4-G	E_{HCOO}
Os-N_4-Gra	-2.93	Hf-N_4-Gra	-3.56
Ru-N_4-Gra	-2.87	Zr-N_4-Gra	-3.37
Re-N_4-Gra	-2.81	Nb-N_4-Gra	-3.23
W-N_4-Gra	-2.54	W-N_4-Gra	-3.21
Fe-N_4-Gra	-2.49	Ta-N_4-Gra	-3.07
Mn-N_4-Gra	-2.48	Y-N_4-Gra	-2.95
Mo-N_4-Gra	-2.45	Ti-N_4-Gra	-2.86
Cr-N_4-Gra	-2.44	Mo-N_4-Gra	-2.84
V-N_4-Gra	-2.21	Sc-N_4-Gra	-2.81
Ta-N_4-Gra	-2.17	V-N_4-Gra	-2.62
Nb-N_4-Gra	-2.02	Re-N_4-Gra	-2.51
Hf-N_4-Gra	-1.77	Cr-N_4-Gra	-1.99
Ti-N_4-Gra	-1.65	Mn-N_4-Gra	-1.39
Ir-N_4-Gra	-1.53	Cd-N_4-Gra	-0.96
Zr-N_4-Gra	-1.43	Fe-N_4-Gra	-0.79
Ag-N_4-Gra	-1.28	Os-N_4-Gra	-0.77
Co-N_4-Gra	-1.05	Ru-N_4-Gra	-0.66
Y-N_4-Gra	-1.03	Zn-N_4-Gra	-0.50
Sc-N_4-Gra	-0.96	Co-N_4-Gra	-0.31
Rh-N_4-Gra	-0.91	Rh-N_4-Gra	-0.13
Cd-N_4-Gra	-0.29	Ag-N_4-Gra	-0.05
Cu-N_4-Gra	-0.26	Ir-N_4-Gra	-0.05
Zn-N_4-Gra	-0.18	Cu-N_4-Gra	0.46
Pd-N_4-Gra	-0.11	Au-N_4-Gra	0.46
Ni-N_4-Gra	-0.05	Ni-N_4-Gra	0.71
Pt-N_4-Gra	-0.04	Pd-N_4-Gra	0.97
Au-N_4-Gra	0.04	Pt-N_4-Gra	1.08

Table S3 Summary of valence-electron number S_{v1}, S_{v2} and S_{v3} of transition metal dopant and nitrogen atom, the electronegativity χ_1, χ_2 and χ_3 of transition metal element and nitrogen atom, and descriptor ψ for MX-N_6-Gra.

MX-N_6-Gra	S_{v1}	S_{v2}	S_{v3}	χ_1	χ_2	χ_3	ψ
OsSc-N_6-Gra	8	3	5	2.2	1.36	3.04	9.37
OsY-N_6-Gra	8	3	5	2.2	1.22	3.04	9.50
OsTi-N_6-Gra	8	4	5	2.2	1.54	3.04	9.92
OsV-N_6-Gra	8	5	5	2.2	1.63	3.04	10.41
OsCr-N_6-Gra	8	6	5	2.2	1.66	3.04	10.87
OsRe-N_6-Gra	8	7	5	2.2	1.9	3.04	11.11
OsOs-N_6-Gra	8	8	5	2.2	2.2	3.04	11.27
OsMn-N_6-Gra	8	7	5	2.2	1.55	3.04	11.40
OsPt-N_6-Gra	8	10	5	2.2	2.28	3.04	11.87
OsPd-N_6-Gra	8	10	5	2.2	2.2	3.04	11.93
OsNi-N_6-Gra	8	10	5	2.2	1.91	3.04	12.14
OsAg-N_6-Gra	8	11	5	2.2	1.93	3.04	12.41
OsCu-N_6-Gra	8	11	5	2.2	1.9	3.04	12.44
OsCd-N_6-Gra	8	12	5	2.2	1.69	3.04	12.90
OsZn-N_6-Gra	8	12	5	2.2	1.65	3.04	12.94
RuSc-N_6-Gra	8	3	5	2.2	1.36	3.04	9.37
RuY-N_6-Gra	8	3	5	2.2	1.22	3.04	9.50
RuTi-N_6-Gra	8	4	5	2.2	1.54	3.04	9.92
RuV-N_6-Gra	8	5	5	2.2	1.63	3.04	10.41
RuCr-N_6-Gra	8	6	5	2.2	1.66	3.04	10.87
RuRe-N_6-Gra	8	7	5	2.2	1.9	3.04	11.11
RuOs-N_6-Gra	8	8	5	2.2	2.2	3.04	11.28
RuMn-N_6-Gra	8	7	5	2.2	1.55	3.04	11.40
RuCo-N_6-Gra	8	9	5	2.2	1.88	3.04	11.85
RuPt-N_6-Gra	8	10	5	2.2	2.28	3.04	11.87
RuPd-N_6-Gra	8	10	5	2.2	2.2	3.04	11.93
RuNi-N_6-Gra	8	10	5	2.2	1.91	3.04	12.14
RuAg-N_6-Gra	8	11	5	2.2	1.93	3.04	12.41
RuCu-N_6-Gra	8	11	5	2.2	1.9	3.04	12.44
RuZn-N_6-Gra	8	12	5	2.2	1.65	3.04	12.94
FeSc-N_6-Gra	8	3	5	1.83	1.36	3.04	9.59
FeY-N_6-Gra	8	3	5	1.83	1.22	3.04	9.72
FeTi-N_6-Gra	8	4	5	1.83	1.54	3.04	10.15
FeV-N_6-Gra	8	5	5	1.83	1.63	3.04	10.65
FeCr-N_6-Gra	8	6	5	1.83	1.66	3.04	11.12
FeRe-N_6-Gra	8	7	5	1.83	1.9	3.04	11.37

FeMn-N_6-Gra	8	7	5	1.83	1.55	3.04	11.66
FeFe-N_6-Gra	8	8	5	1.83	1.83	3.04	11.81
FeRh-N_6-Gra	8	9	5	1.83	2.28	3.04	11.83
FeCo-N_6-Gra	8	9	5	1.83	1.88	3.04	12.12
FePt-N_6-Gra	8	10	5	1.83	2.28	3.04	12.15
FePd-N_6-Gra	8	10	5	1.83	2.2	3.04	12.20
FeNi-N_6-Gra	8	10	5	1.83	1.91	3.04	12.42
FeAg-N_6-Gra	8	11	5	1.83	1.93	3.04	12.70
FeCu-N_6-Gra	8	11	5	1.83	1.9	3.04	12.73
FeZu-N_6-Gra	8	11	5	1.83	2.54	3.04	13.24

Table S4 The adsorption energy of *CO, *COOH and *HCOO on MX-N_6-Gra.

MX-N_6-Gra	E_{CO}	E_{COOH}	E_{HCOO}
OsSc-N_6-Gra	-2.33	-3.44	-3.75
OsY-N_6-Gra	-2.23	-3.37	-3.74
OsTi-N_6-Gra	-1.99	-3.31	-3.66
OsV-N_6-Gra	-1.91	-3.05	-3.41
OsCr-N_6-Gra	-1.67	-2.60	-3.26
OsRe-N_6-Gra	-1.81	-2.97	-3.54
OsOs-N_6-Gra	-1.65	-2.78	-2.35
OsMn-N_6-Gra	-1.47	-2.24	-1.73
OsPt-N_6-Gra	-1.42	-2.63	-2.05
OsPd-N_6-Gra	-1.38	-2.48	-1.97
OsNi-N_6-Gra	-1.35	-2.43	-1.98
OsAg-N_6-Gra	-1.08	-2.28	-2.25
OsCu-N_6-Gra	-1.36	-2.42	-2.30
OsCd-N_6-Gra	-1.12	-1.94	-3.48
OsZn-N_6-Gra	-1.06	-2.04	-3.04
RuSc-N_6-Gra	-2.28	-3.49	-4.18
RuY-N_6-Gra	-2.15	-3.43	-4.06
RuTi-N_6-Gra	-1.87	-3.40	-4.05
RuV-N_6-Gra	-1.76	-2.51	-3.64
RuCr-N_6-Gra	-1.43	-2.57	-3.10
RuRe-N_6-Gra	-1.48	-2.75	-3.46
RuOs-N_6-Gra	-1.31	-2.62	-2.52
RuMn-N_6-Gra	-1.28	-2.16	-2.06
RuCo-N_6-Gra	-1.22	-2.56	-2.26
RuPt-N_6-Gra	-1.36	-2.41	-2.06
RuPd-N_6-Gra	-1.34	-2.34	-2.00
RuNi-N_6-Gra	-1.14	-2.39	-2.09
RuAg-N_6-Gra	-1.00	-2.29	-2.46
RuCu-N_6-Gra	-1.38	-2.40	-2.27
RuZn-N_6-Gra	-1.19	-2.10	-2.66
FeSc-N_6-Gra	-1.79	-3.23	-3.91
FeY-N_6-Gra	-1.81	-3.18	-4.02
FeTi-N_6-Gra	-1.76	-3.91	-4.41
FeV-N_6-Gra	-1.48	-2.91	-3.48
FeCr-N_6-Gra	-1.28	-2.56	-3.44
FeRe-N_6-Gra	-1.06	-2.26	-3.00
FeMn-N_6-Gra	-1.14	-1.85	-2.35
FeFe-N_6-Gra	-1.14	-2.35	-2.44
FeRh-N_6-Gra	-1.04	-2.43	-2.21
FeCo-N_6-Gra	-1.05	-2.34	-2.24

FePt-N_6-Gra	-1.29	-2.28	-2.17
FePd-N_6-Gra	-1.31	-2.28	-2.26
FeNi-N_6-Gra	-1.25	-2.35	-2.35
FeAg-N_6-Gra	-1.31	-2.41	-2.86
FeCu-N_6-Gra	-1.48	-2.42	-2.62
FeZu-N_6-Gra	-1.64	-2.46	-3.23

Table S5 Reaction free energy for CO_2 reduction to HCOOH at zero applied voltage (vs RHE) and 298 K and overpotential on different catalysts in the gas phase.

MX-N_6-Gra	CO_2→*HCOO (eV)	*HCOO→*HCOOH (eV)	*HCOOH→HCOOH (eV)	*+H→ *H(eV)	η (V)
OsZn-N_6-Gra	0.11	-0.11	0.18	0.39	-0.09
RuZn-N_6-Gra	0.38	-0.46	0.25	0.47	0.18
FeZn-N_6-Gra	-0.03	0.78	-0.56	0.22	0.58

Table S6 Reaction free energy for CO_2 reduction to CO at zero applied voltage (vs RHE) and 298 K and overpotential on different atomic catalysts in the gas phase.

MX-N_6-Gra	CO_2→*COOH(eV)	*COOH→*CO(eV)	*CO→CO(eV)	*+H→H(eV)	η (V)
OsPd-N_6-Gra	0.41	-0.54	0.80	0.01	0.30
RuCo-N_6-Gra	0.36	-0.28	0.57	-0.06	0.25
RuNi-N_6-Gra	0.51	-0.38	0.53	0.14	0.40
RuAg-N_6-Gra	0.56	-0.28	0.37	0.21	0.45
RuCu-N_6-Gra	0.40	-0.44	0.70	0.11	0.29
FeRh-N_6-Gra	0.49	-0.28	0.44	0.17	0.38
FeCo-N_6-Gra	0.49	-0.31	0.47	0.20	0.38
FePd-N_6-Gra	0.54	-0.60	0.71	0.28	0.43
FePt-N_6-Gra	0.51	-0.63	0.77	0.33	0.40
PdRu-N_6-Gra	0.48	-0.58	0.77	0.11	0.37

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