Supplementary Material

Investigation of dual atom doped single-layer MoS_2 for electrochemical reduction of carbon dioxide by first-principle calculations and machine-learning

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The formation formula of each C1 product, the zpe-point energy (ZPE), the entropy change (TS), adsorption structures of different CO_2RR intermediates on MoS_2, computed Gibbs free energies of every CO_2RR intermediates, the changes in the reaction free energy (ΔG), the density of states (DOS) of *CO and Calculation of adsorption free energy of key intermediates, Gibbs free energy of adsorbed water, and water dissociation.

The scaling relations of transition metal surfaces were mainly reported by Norskov et al, the adsorption energies of *COOH, *CO and *CHO were calculated in order to compare the scaling relations of dual atom catalysts with that of transition-metals. Based on Nørskov *et al.*'s theory[1], the adsorption energies of *COOH, *CO, and *CHO were calculated with the following equations:

$$E_{ads}(COOH) = E(*COOH) - E(*H_2O) - E\big(CO_2(g)\big) - 1/2\,E(H_2)$$
$$E_{ads}(CO) = E(*CO) - E(*H_2O) - E\big(CO(g)\big)$$
$$E_{ads}(CHO) = E(*CHO) - E(*H_2O) - E\big(CO(g)\big) - 1/2\,E(H_2)$$

Where E_{ads}(COOH), E_{ads}(CO) and E_{ads}(CHO) are the adsorption energies of *COOH, *CO, and *CHO, respectively. In particular, E(*H_2O) represents the adsorption energy of the water molecule.

The mechanism of CO_2 reduction is:
The formula for HCOOH formation:

$$CO_2 + H^+ + e^- \rightarrow *HCOO \quad (1)$$

$$*HCOO + H^+ + e^- \rightarrow *HCOOH \quad (2)$$

$$*HCOOH \rightarrow HCOOH + * \quad (3)$$

The formula for CO formation:

$$CO_2 + H^+ + e^- \rightarrow *COOH \quad (4)$$

$$*COOH + H^+ + e^- \rightarrow *CO + H_2O \quad (5)$$

$$*CO \rightarrow CO + * \quad (6)$$

The formula for HCHO formation:

$$*CO + H^+ + e^- \rightarrow *CHO \quad (7)$$

$$*CHO + H^+ + e^- \rightarrow *OCH_2 \quad (8)$$

$$*OCH_2 \rightarrow HCHO + * \quad (9)$$

The formula for CH_3OH formation:

$$*OCH_2 + H^+ + e^- \rightarrow *OCH_3 \quad (10)$$

$$*OCH_3 + H^+ + e^- \rightarrow *CH_3OH \quad (11)$$

$$*CH_3OH \rightarrow CH_3OH + * \quad (12)$$

The formula for CH_4 formation:

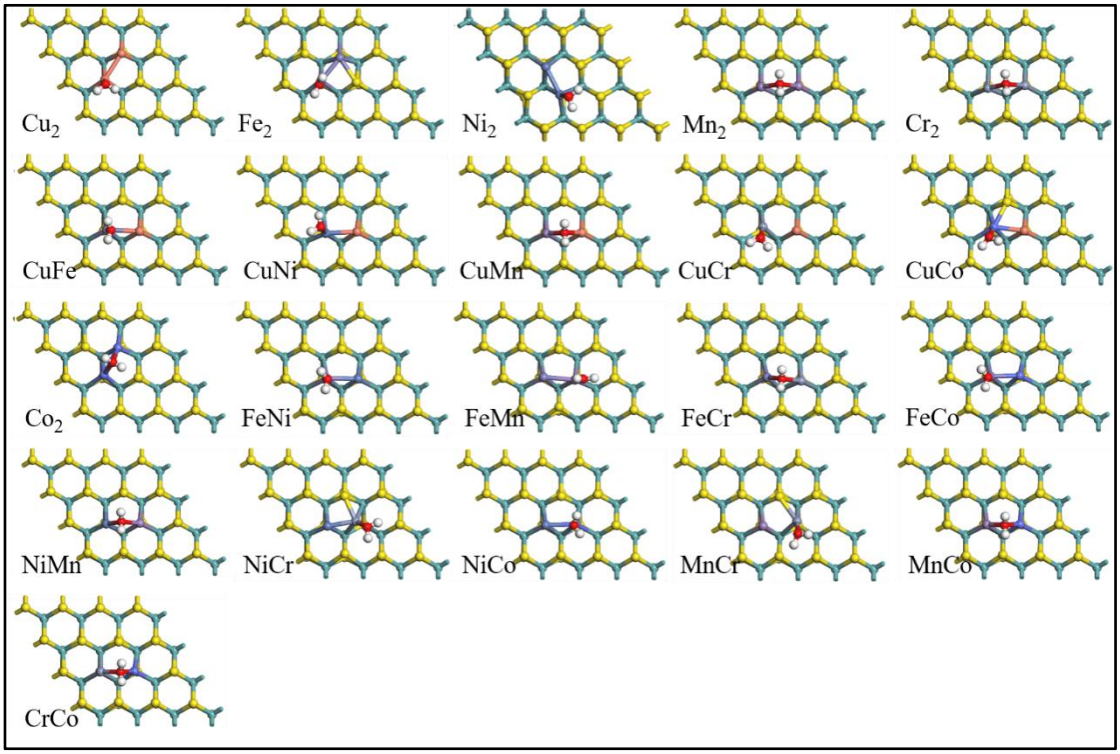
$$*OCH_3 + H^+ + e^- \rightarrow *OCH_4 \quad (13)$$

$$*OCH_4 + H^+ + e^- \rightarrow *O + CH_4 \quad (14)$$

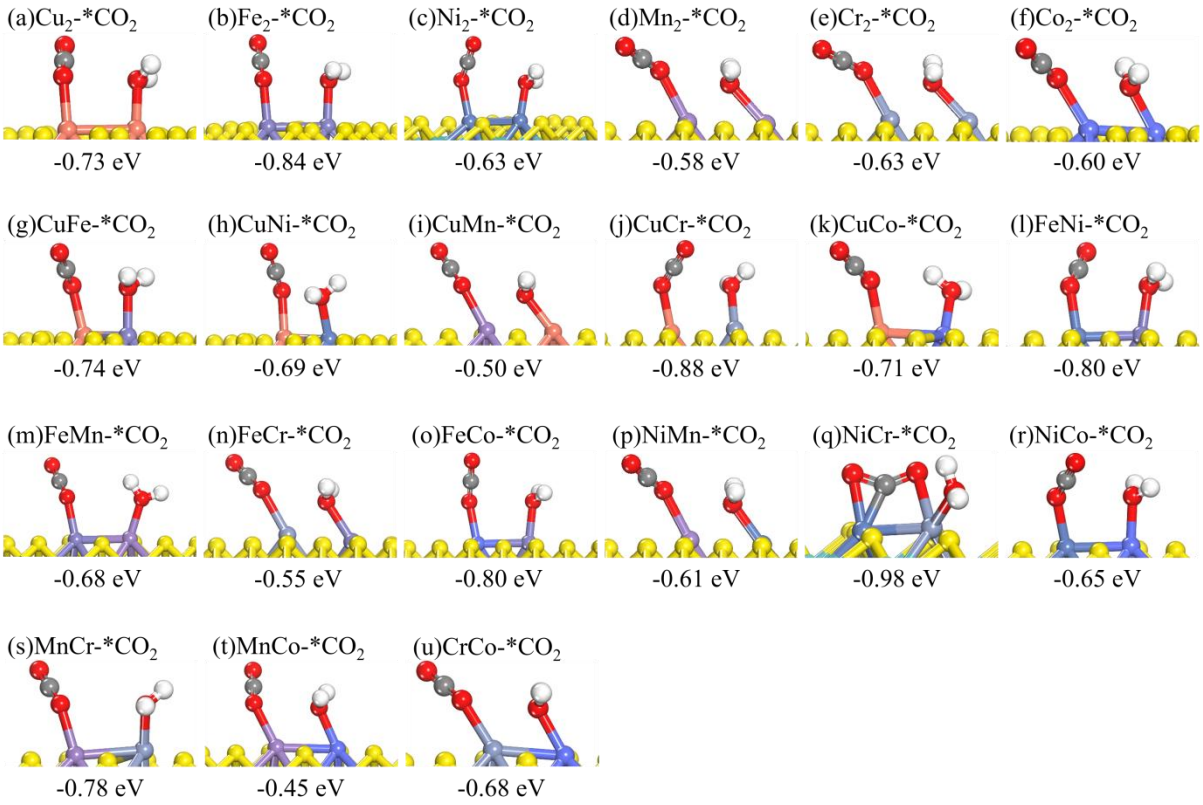
$$*O + H^+ + e^- \rightarrow *OH \quad (15)$$

$$*OH + H^+ + e^- \rightarrow *H_2O \quad (16)$$

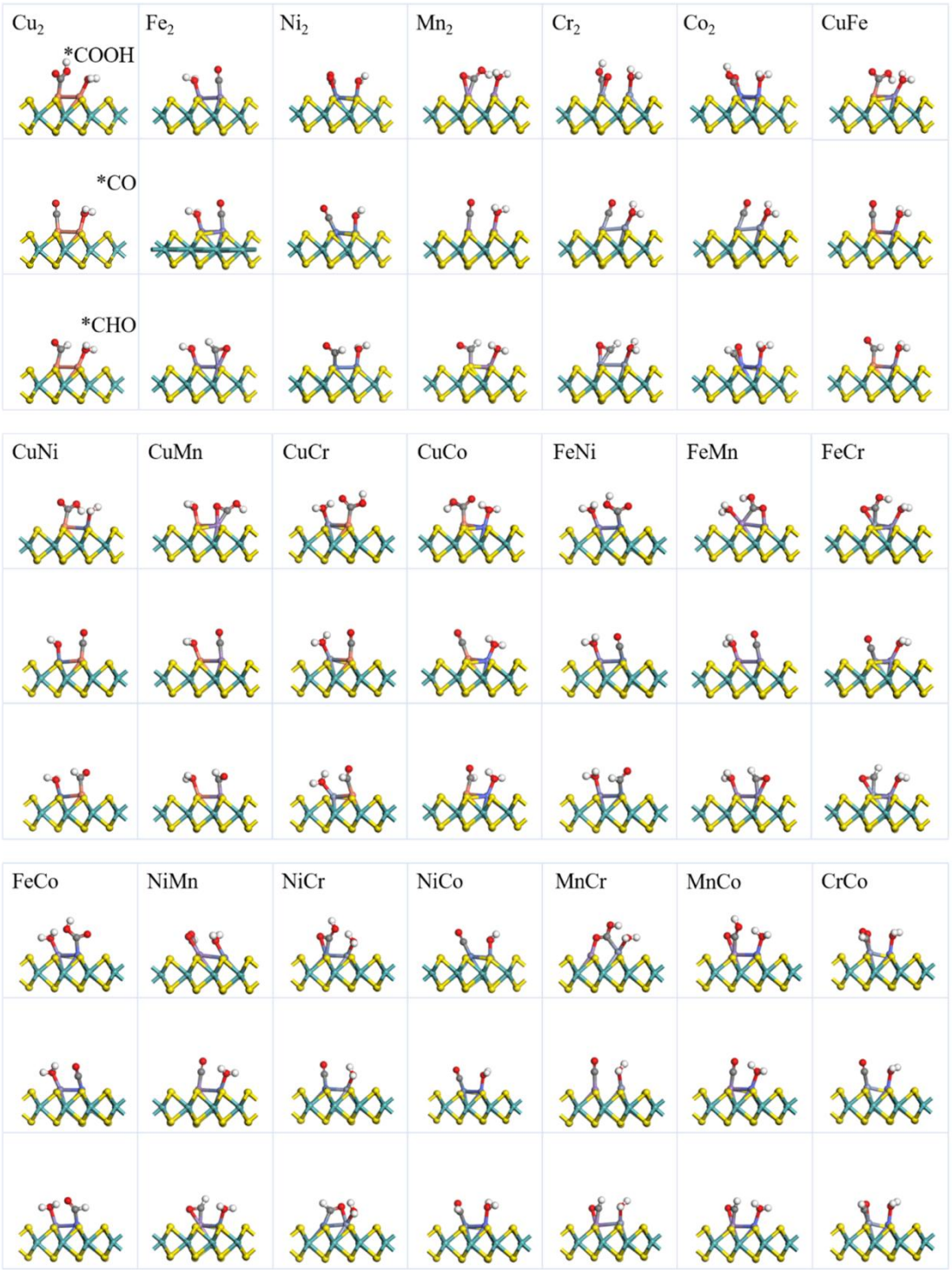
$$*H_2O \rightarrow H_2O + * \quad (17)$$



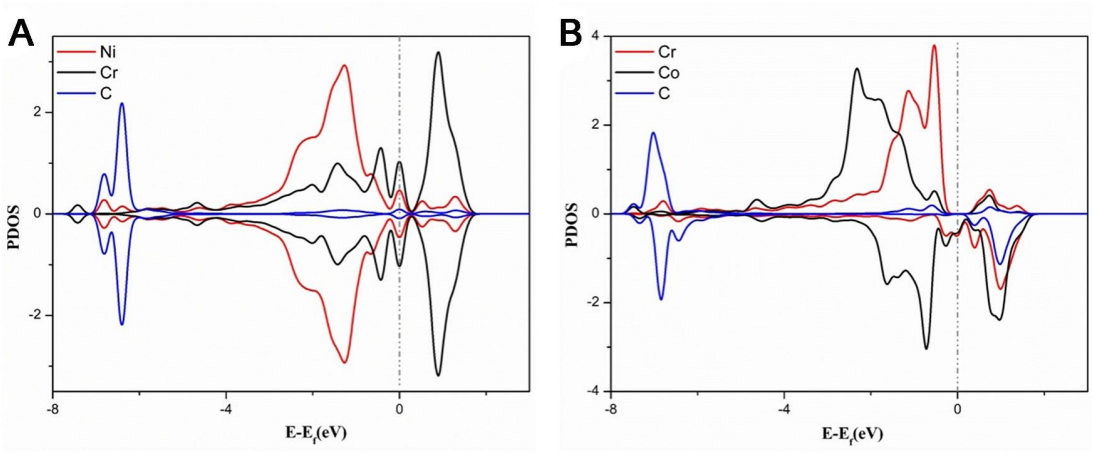
Supplementary Figure 1. Optimized structures of 6 homonuclear MoS_2-M_2 and 15 heteronuclear MoS_2-M_1M_2 with adsorbed water molecule.



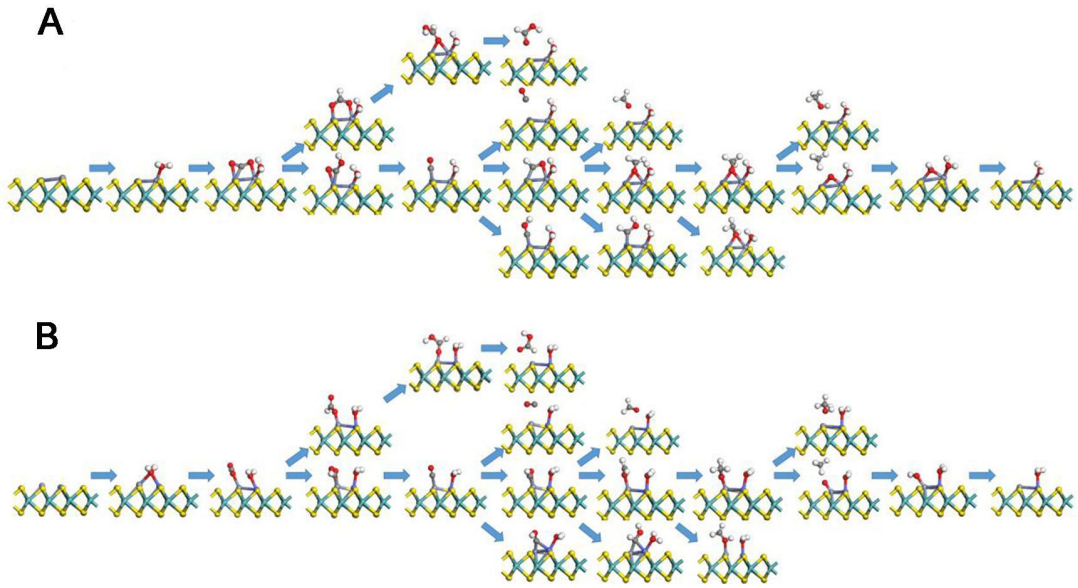
Supplementary Figure 2. The most stable structure of *CO_2 adsorbed on 6 homonuclear and 15 heteronuclear DACs. The numbers in the figure indicate their adsorption energies.



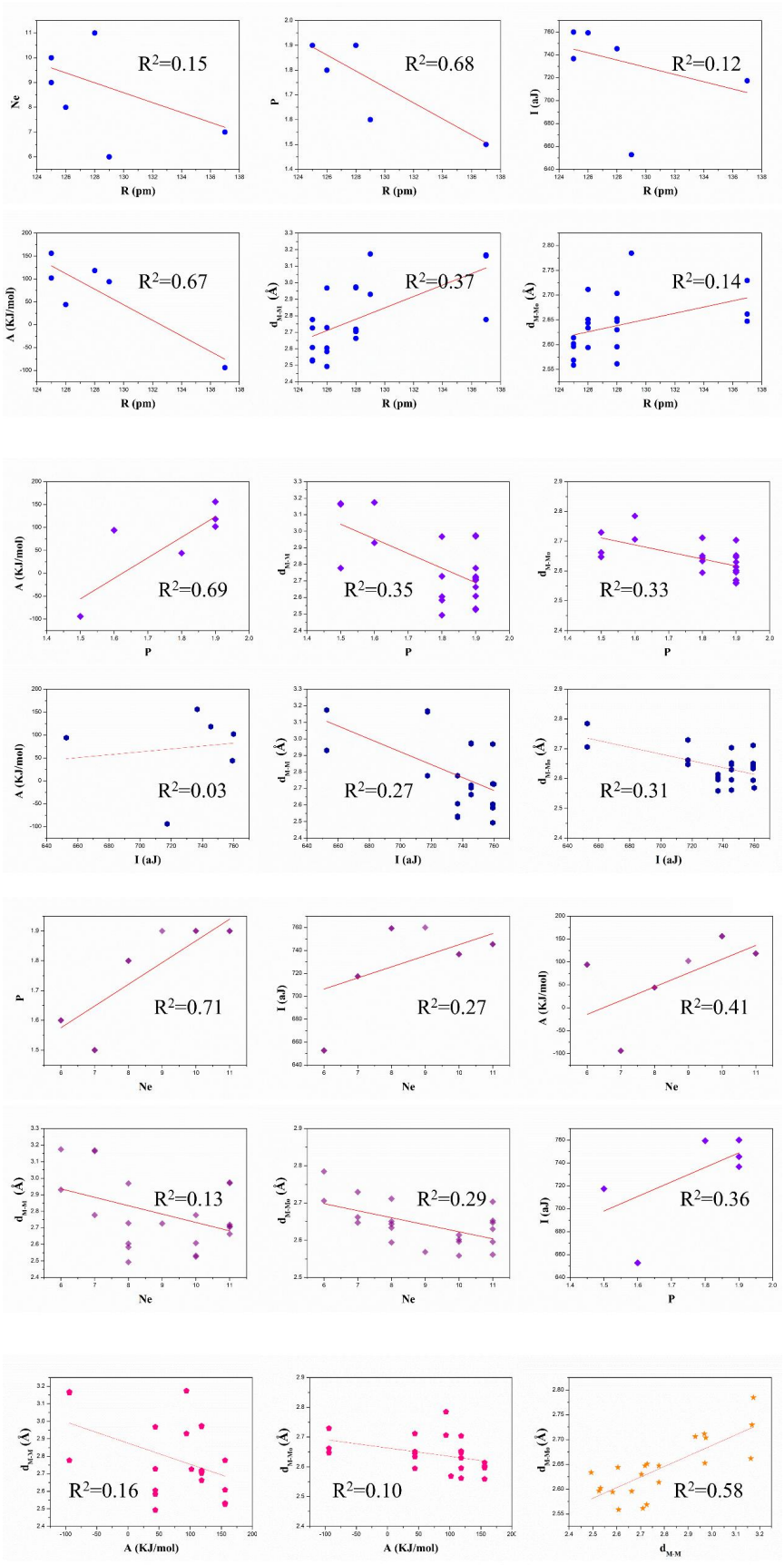
Supplementary Figure 3. Optimized geometries of *COOH, *CO and *CHO adsorbed on MoS_2-M_2/M_1M_2 DACs.



Supplementary Figure 4. The projected density of states of MoS_2-NiCr and MoS_2-CrCo systems after CO adsorption.



Supplementary Figure 5. Optimized intermediate structures along all possible CO_2RR pathways towards various C1 products on (A) MoS_2-NiCr and (B) MoS_2-CrCo.



Supplementary Figure 6. The correlation between different factors (R, Ne, P, I, A, d_{M-M} and d_{M-Mo}).

Supplementary Table 1. Free energy corrections for gas molecules (H_2, CO, CO_2, H_2O, CH_4, CH_3OH, HCOOH, HCHO) (In addition, we added -0.34 eV corrections for CO and +0.10 eV corrections for CO_2 due to the inaccurate description of CO_2 and CO molecules by the PBE function.)

Molecule	**E***	**E_{ZPE}**	**TS**	**G**
CO_2	-5128.69	0.31	0.66	-5129.94
CO	-3081.13	0.13	0.61	-3081.95
H_2	-31.57	0.27	0.4	-31.70
H_2O	-2077.99	0.57	0.67	-2078.09
HCOOH	-5160.27	0.9	0.99	-5160.36
HCHO	-3113.51	0.72	0.68	-3113.47
CH_3OH	-3146.32	1.38	0.81	-3145.75
CH_4	-1100.77	1.2	0.58	-1100.15

Supplementary Table 2. The formation energies of metal dimers embedded in MoS_2.

Species	E_f(eV)	Species	E_f(eV)
Cu_2	-4.97	**FeNi**	-6.05
Fe_2	-6.00	**FeMn**	-5.62
Ni_2	-6.12	**FeCr**	-5.46
Mn_2	-5.28	**FeCo**	-6.12
Cr_2	-4.92	**NiMn**	-5.71
Co_2	-6.16	**NiCr**	-5.29
CuFe	-5.46	**NiCo**	-6.16
CuNi	-5.54	**MnCr**	-5.11
CuMn	-5.14	**MnC**	-5.74
CuCr	-4.97	**CrCo**	-5.58
CuCo	-5.49		

Supplementary Table 3. Comparison of Gibbs adsorption free energies of adsorbed CO_2 and adsorbed water molecule.

Species	**ΔG(*CO_2)**	**ΔG(*H_2O)**	**Species**	**ΔG(*CO_2)**	**ΔG(*H_2O)**
Cu_2	0.17	-0.73	FeNi	-0.48	-0.85
Fe_2	-0.68	-0.75	FeMn	-0.78	-0.86
Ni_2	-0.17	-0.75	FeCr	-0.89	-1.08
Mn_2	-0.74	-1.16	FeCo	-0.63	-0.86
Cr_2	-1.14	-1.17	NiMn	-0.41	-1.05
Co_2	0.00	-1.04	NiCr	-0.67	-1.01
CuFe	-0.43	-0.98	NiCo	-0.51	-1.00
CuNi	-0.21	-0.73	MnCr	-0.93	-0.86
CuMn	-0.33	-1.03	MnCo	-0.77	-1.13
CuCr	-0.51	-0.81	CrCo	-0.96	-1.10
CuCo	-0.51	-0.88			

Supplementary Table 4. The reaction free energy for the dissociation of adsorbed H_2O into H* and OH*.

Species	G(*H_2O)	G(*H + *OH)	ΔG
Cu_2	-380801.58	-380800.52	1.07
Fe_2	-376487.64	-376487.18	0.46
Ni_2	-379224.26	-379223.39	0.87
Mn_2	-375322.20	-375321.44	0.76
Cr_2	-374311.35	-374311.02	0.33
Co_2	-377772.33	-377771.54	0.79
CuFe	-378644.80	-378644.33	0.47
CuNi	-380012.90	-380011.85	1.06
CuMn	-378062.01	-378061.45	0.56
CuCr	-377556.37	-377556.09	0.28
CuCo	-379286.78	-379286.44	0.34
FeNi	-377856.04	-377855.41	0.63
FeMn	-375904.79	-375904.44	0.35
FeCr	-375399.62	-375399.33	0.29
FeCo	-377130.04	-377129.56	0.48
NiMn	-377273.35	-377272.68	0.67
NiCr	-376767.40	-376766.83	0.57
NiCo	-378498.44	-378497.41	1.04
MnCr	-374816.51	-374816.17	0.34
MnCo	-376547.34	-376546.74	0.60
CrCo	-376041.90	-376041.30	0.60

Supplementary Table 5. The adsorption energies of intermediates (*COOH, *CO, *CHO).

Species	E_{ads}(*COOH)	E_{ads}(*CO)	E_{ads}(*CHO)
Cu_2	-0.22	-1.44	-0.69
Fe_2	-0.60	-1.68	-1.18
Ni_2	-0.29	-1.87	-0.91
Mn_2	0.03	-1.02	0.59
Cr_2	-0.22	-1.34	-0.95
Co_2	-0.34	-1.77	-1.32
CuFe	-0.29	-1.38	-0.39
CuNi	-0.19	-1.43	-0.78
CuMn	-0.04	-1.05	-0.39
CuCr	-0.55	-1.44	-0.61
CuCo	-0.36	-1.41	-0.73
FeNi	-0.58	-1.91	-1.02
FeMn	-0.81	-1.70	-1.19
FeCr	-0.48	-1.39	-0.79
FeCo	-0.68	-2.14	-1.04
NiMn	0.12	-1.05	-0.74
NiCr	-0.66	-2.01	-1.75
NiCo	-0.56	-1.92	-1.22
MnCr	-0.83	-1.29	-0.98
MnCo	-0.21	-1.11	-0.79
CrCo	-0.48	-1.14	-1.12

Supplementary Table 6. 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 on MoS_2-NiCr and MoS_2-CrCo during electrochemical CO_2RR.

E_*(MoS_2-NiCr)	Absorbate	E_{*ads}	E_{ZPE}	TS	G	ΔG
374688.30	***H_2O**	376767.99	0.68	0.08	376767.40	-1.01
	***CO_2**	381897.51	0.31	0.12	381897.32	-0.98
	***COOH**	381913.12	0.58	0.14	381912.69	0.48
	***CO**	379851.13	0.20	0.04	379850.97	-0.52
	***CHO**	379866.66	0.47	0.08	379866.26	0.56
	***COH**	379865.35	0.47	0.05	379864.93	1.89
	***OCH_2**	379882.73	0.79	0.10	379882.04	0.07
	***CHOH**	379882.03	0.78	0.10	379881.35	0.76
	***OCH_3**	379900.01	1.10	0.08	379898.99	-1.10
	***CH_2OH**	379899.62	1.20	0.12	379898.54	-0.65
	***O + CH_4(g)**	378815.34	0.08	0.05	378815.31	-0.62
	***CH_3OH**	379915.57	1.44	0.12	379914.25	0.59
	***OH**	378831.53	0.38	0.06	378831.21	-0.05
	***H_2O**	378847.06	0.67	0.10	378846.48	0.58
	***HCOO**	381914.19	0.64	0.19	381913.74	-0.57
	***HCOOH**	381929.36	0.89	0.22	381928.68	0.91
	***H**	376784.26	0.19	0.01	376784.07	-0.82

$E_{*}(MoS_2\text{-}CrCo)$	Absorbate	E_{*ads}	E_{ZPE}	TS	G	ΔG
373962.71	$*H_2O$	376042.44	0.67	0.13	376041.90	-1.10
	$*CO_2$	381171.68	0.31	0.16	381171.53	-0.68
	*COOH	381187.40	0.62	0.15	381186.94	0.44
	*CO	379124.71	0.16	0.16	379124.70	-0.01
	*CHO	379140.48	0.46	0.11	379140.13	0.43
	*COH	379139.44	0.47	0.11	379139.08	1.48
	$*OCH_2$	379156.98	0.78	0.05	379156.24	-0.27
	*CHOH	379156.24	0.77	0.13	379155.59	0.38
	$*OCH_3$	379173.75	1.10	0.08	379172.73	-0.63
	$*CH_2OH$	379171.96	1.05	0.09	379170.99	1.43
	$*O + CH_4(g)$	378089.34	0.07	0.04	378089.31	-0.88
	$*CH_3OH$	379190.01	1.43	0.22	379188.80	-0.22
	*OH	378105.34	0.35	0.11	378105.11	0.05
	$*H_2O$	378121.27	0.68	0.07	378120.67	0.29
	*HCOO	381187.92	0.58	0.16	381187.49	-0.11
	*HCOOH	381204.04	0.92	0.18	381203.30	0.04
	*H	376058.36	0.18	0.01	376058.20	-0.45

Supplementary Table 7. Comparison of adsorption energy of *H_2O, *CO_2 and *H.

Structure	**ΔG(*H_2O)**	**ΔG(*CO_2)**	**ΔG(*H)**
Cu_2	-0.73	-0.73	-0.63
Fe_2	-0.75	-0.84	-0.86
Ni_2	-0.75	-0.63	-0.49
Mn_2	-1.16	-0.58	0.30
Cr_2	-1.17	-0.63	0.08
Co_2	-1.04	-0.60	-0.66
CuFe	-0.98	-0.74	-0.62
CuNi	-0.73	-0.69	-0.66
CuMn	-1.03	-0.50	-0.56
CuCr	-0.81	-0.88	-0.79
CuCo	-0.88	-0.71	-0.63
FeNi	-0.85	-0.80	-0.70
FeMn	-0.86	-0.68	-0.72
FeCr	-1.08	-0.55	-0.26
FeCo	-0.86	-0.80	-0.83
NiMn	-1.05	-0.61	-0.25
NiCr	-1.01	-0.98	-0.82
NiCo	-1.00	-0.65	-0.45
MnCr	-0.86	-0.78	-0.72
MnCo	-1.13	-0.45	-0.32
CrCo	-1.10	-0.68	-0.45

Supplementary Table 8. Summarises the distance between two metal atoms (d_{M-M}, Å), the average distance between two metal atoms and Mo atoms (d_{M-Mo}, Å), the radii of two metal atoms (R_1 and R_2, pm), the number of outer electrons of two metal atoms (Ne_1 and Ne_2), the Pauling electronegativity of two metal atoms (P_1 and P_2), the first ionisation energy of two metal atoms (I_1 and I_2, aJ) and the electron affinity energy of two metal atoms (A_1 and A_2, kJ/mol).

Catalyst	R_1	Ne_1	P_1	I_1	A_1	d_{M-M}	d_{M-Mo}	R_2	Ne_2	P_2	I_2	A_2
CuCu	128	11	1.9	745.4	118.3	2.72	2.65	128	11	1.9	745.4	118.3
FeFe	126	8	1.8	759.3	44	2.61	2.64	126	8	1.8	759.3	44
NiNi	125	10	1.9	736.7	156	2.61	2.56	125	10	1.9	736.7	156
MnMn	137	7	1.5	717.4	-94	3.16	2.66	137	7	1.5	717.4	-94
CrCr	129	6	1.6	652.7	94	3.17	2.78	129	6	1.6	652.7	94
CoCo	125	9	1.9	760	102	2.73	2.57	125	9	1.9	760	102
CuFe	128	11	1.9	745.4	118.3	2.70	2.63	126	8	1.8	759.3	44
CuNi	128	11	1.9	745.4	118.3	2.71	2.56	125	10	1.9	736.7	156
CuMn	128	11	1.9	745.4	118.3	2.97	2.65	137	7	1.5	717.4	-94
CuCr	128	11	1.9	745.4	118.3	2.97	2.70	129	6	1.6	652.7	94
CuCo	128	11	1.9	745.4	118.3	2.66	2.60	125	9	1.9	760	102
FeNi	126	8	1.8	759.3	44	2.58	2.59	125	10	1.9	736.7	156
FeMn	12	8	1.	759.	44	2.73	2.65	13	7	1.	717.	-94

	6		8	3				7		5	4	
FeCr	126	8	1.8	759.3	44	2.97	2.71	129	6	1.6	652.7	94
FeCo	126	8	1.8	759.3	44	2.49	2.63	125	9	1.9	760	102
NiMn	125	10	1.9	736.7	156	2.78	2.61	137	7	1.5	717.4	-94
NiCr	125	10	1.9	736.7	156	2.53	2.60	129	6	1.6	652.7	94
NiCo	125	10	1.9	736.7	156	2.53	2.60	125	9	1.9	760	102
MnCr	137	7	1.5	717.4	-94	3.17	2.73	129	6	1.6	652.7	94
MnCo	137	7	1.5	717.4	-94	2.78	2.65	125	9	1.9	760	102
CrCo	129	6	1.6	652.7	94	2.93	2.71	125	9	1.9	760	102

Reference:

1. Chan, K.; Tsai, C.; Hansen, H. A.; Nørskov, J. K., Molybdenum sulfides and selenides as possible electrocatalysts for CO_2 reduction. *ChemCatChem* **2014,** *6* (7), 1899-1905.