Electronic Supplementary Information for

CO_2 electrochemical reduction boosted by the regulated electronic properties of metalloporphyrins through tuning atomic environment

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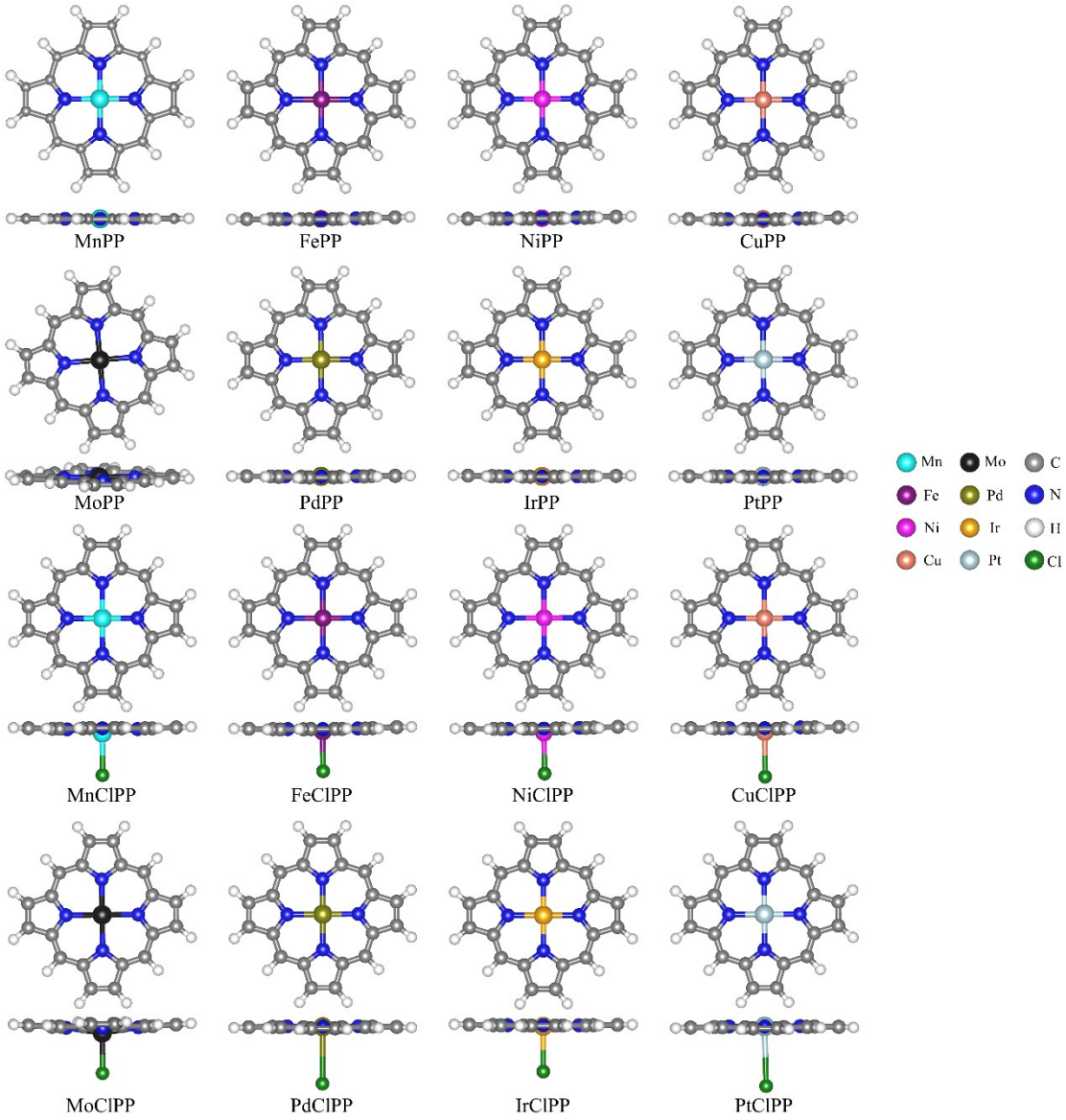

Fig. S1 DFT-optimized structures of MPP and MClPP, where M = Mn, Fe, Ni, Cu, Mo, Pd, Ir and Pt. The cyan, purple, fuchsia, pink, black, olive, orange, lightblue, grey, blue, white and green balls represent Mn, Fe, Ni, Cu, Mo, Pd, Ir, Pt, C, N, H and Cl atoms, respectively.

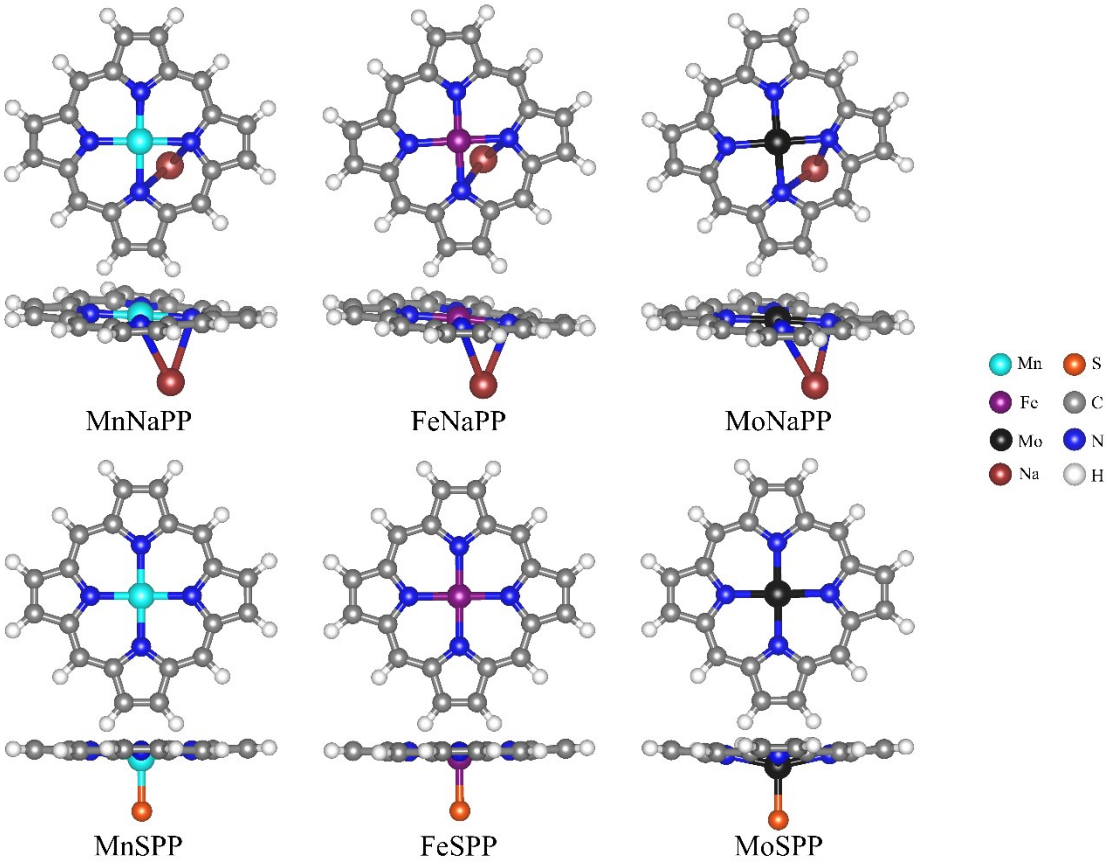

Fig. S2 DFT-optimized structures of MXPP, where M = Mn, Fe, and Mo, X= Na and S. The cyan, purple, black, brown, orangered, grey, blue and white balls represent Mn, Fe, Mo, Na, S, C, N and H atoms, respectively.

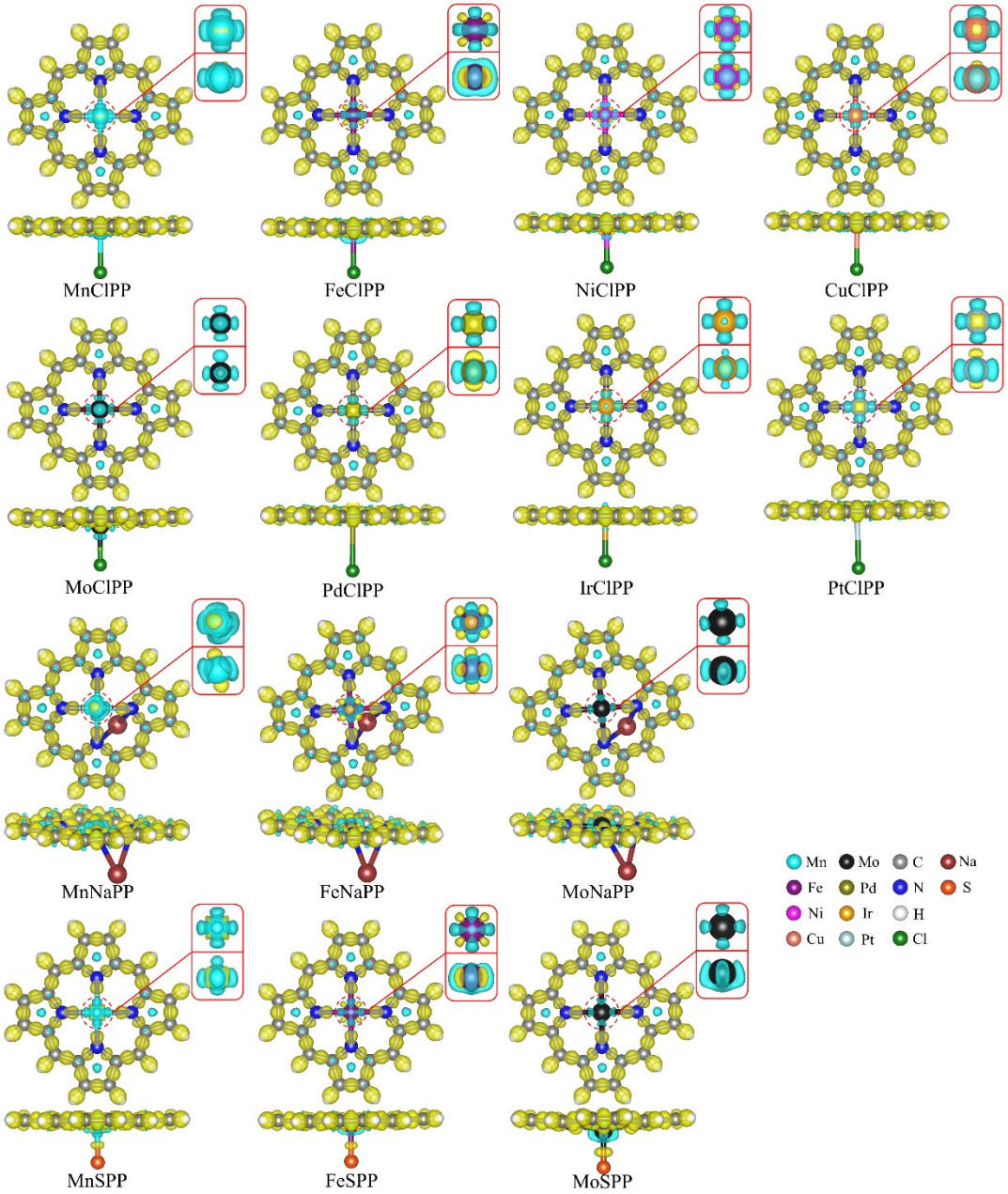

Fig. S3 Top and side views of isosurface of deformation charge density of MPP and MClPP, where M = Mn, Fe, Ni, Cu, Mo, Pd, Ir and Pt. The inset shows the top and side views of the enlarged deformation charge density of the metal sites. The value of isosurface is 0.02 eV/Å^3. The cyan, purple, fuchsia, pink, black, olive, orange, lightblue, grey, blue, white and green balls represent Mn, Fe, Ni, Cu, Mo, Pd, Ir, Pt, C, N, H and Cl atoms, respectively.

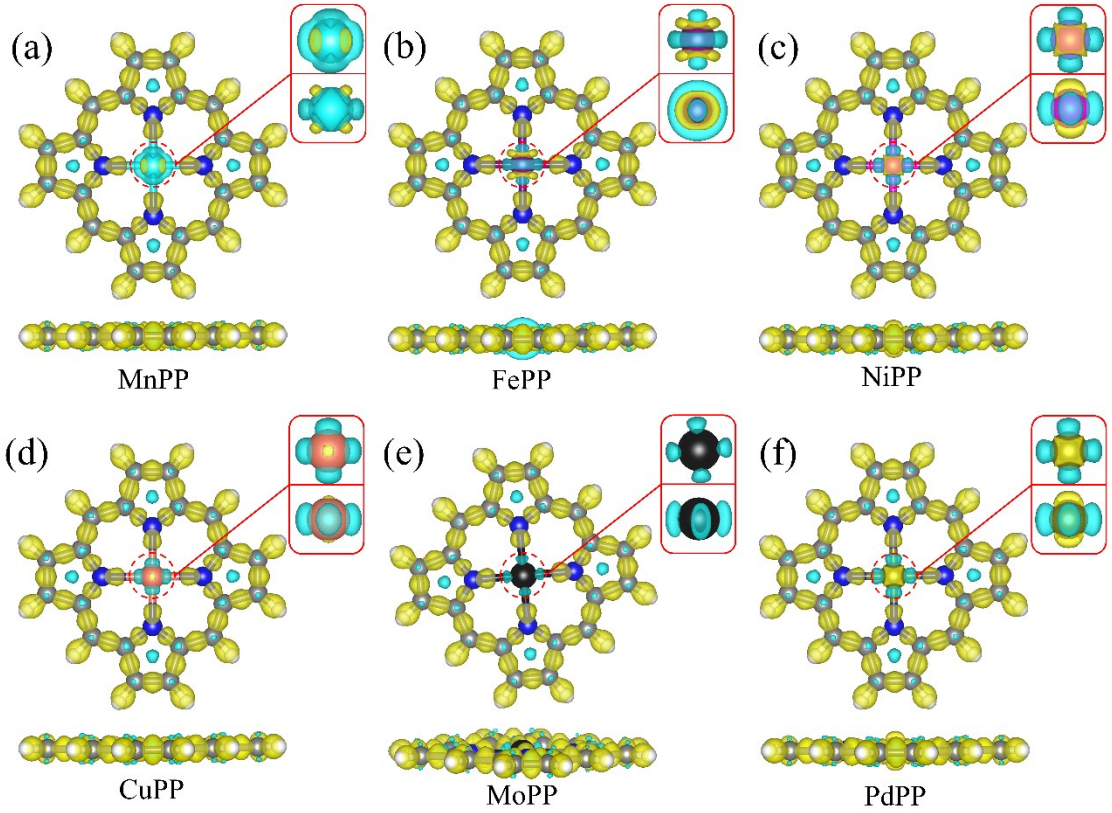

Fig. S4 Top and side views of isosurface of deformation charge density of MNaPP and MSPP, where M = Mn, Fe, and Mo. The inset shows the top and side views of the enlarged deformation charge density of the metal sites. The yellow areas represent charge accumulation and the cyan areas represent charge depletion. The value of isosurface is 0.02 eV/Å^3. The cyan, purple, black, brown, orangered, grey, blue and white balls represent Mn, Fe, Mo, Na, S, C, N and H atoms, respectively.

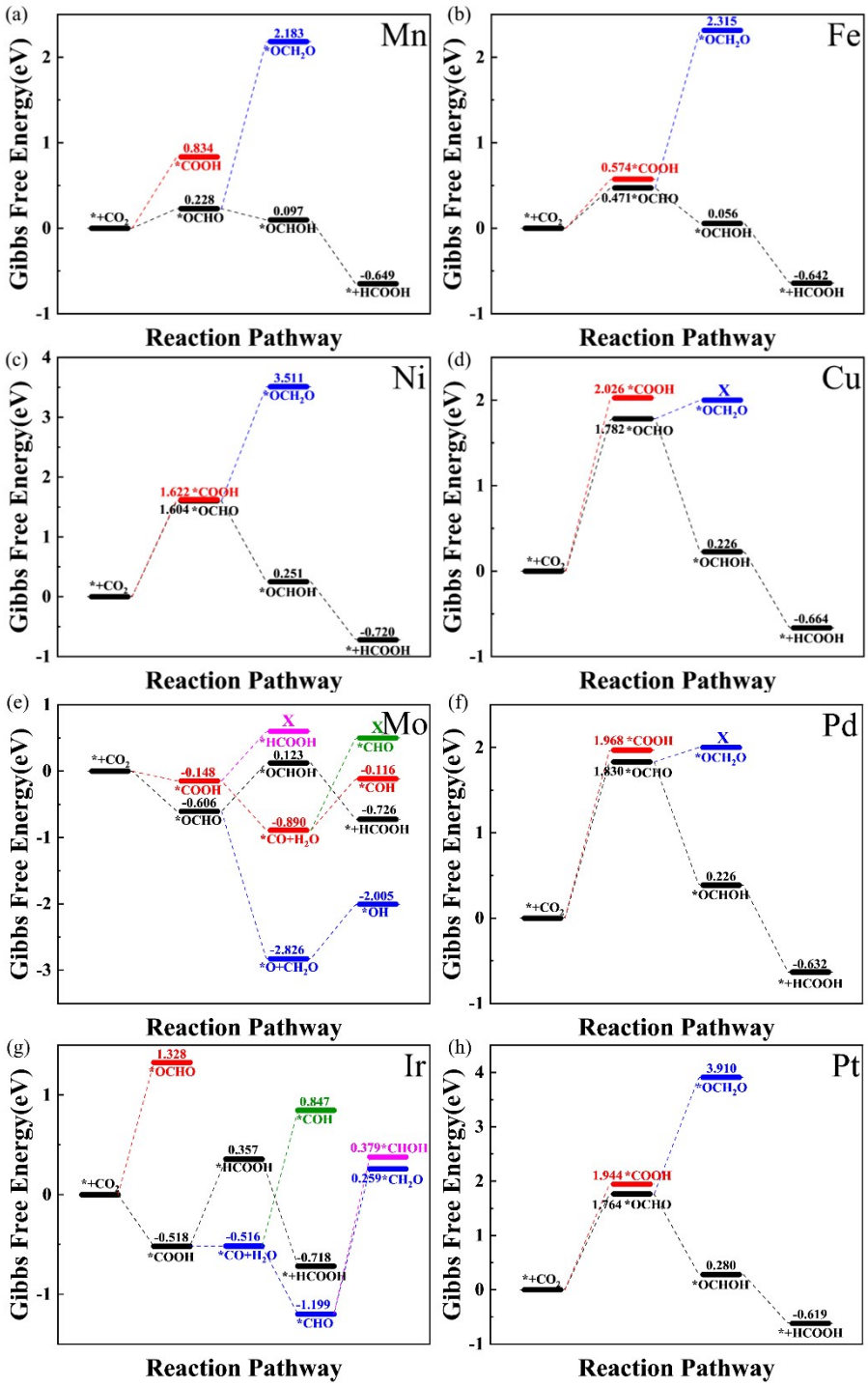

Fig. S5 Gibbs free energy profiles for CO_2RR on (a)MnPP, (b)FePP, (c)NiPP, (d)CuPP, (e)MoPP, (f)PdPP, (g)IrPP and (h)PtPP at zero potential. The free energy zero is set as that of a CO_2 molecule in the gas phase and with a clean catalyst surface. The "X" in the profiles indicates that the intermediate is unstable. The black line is the most favorable pathway.

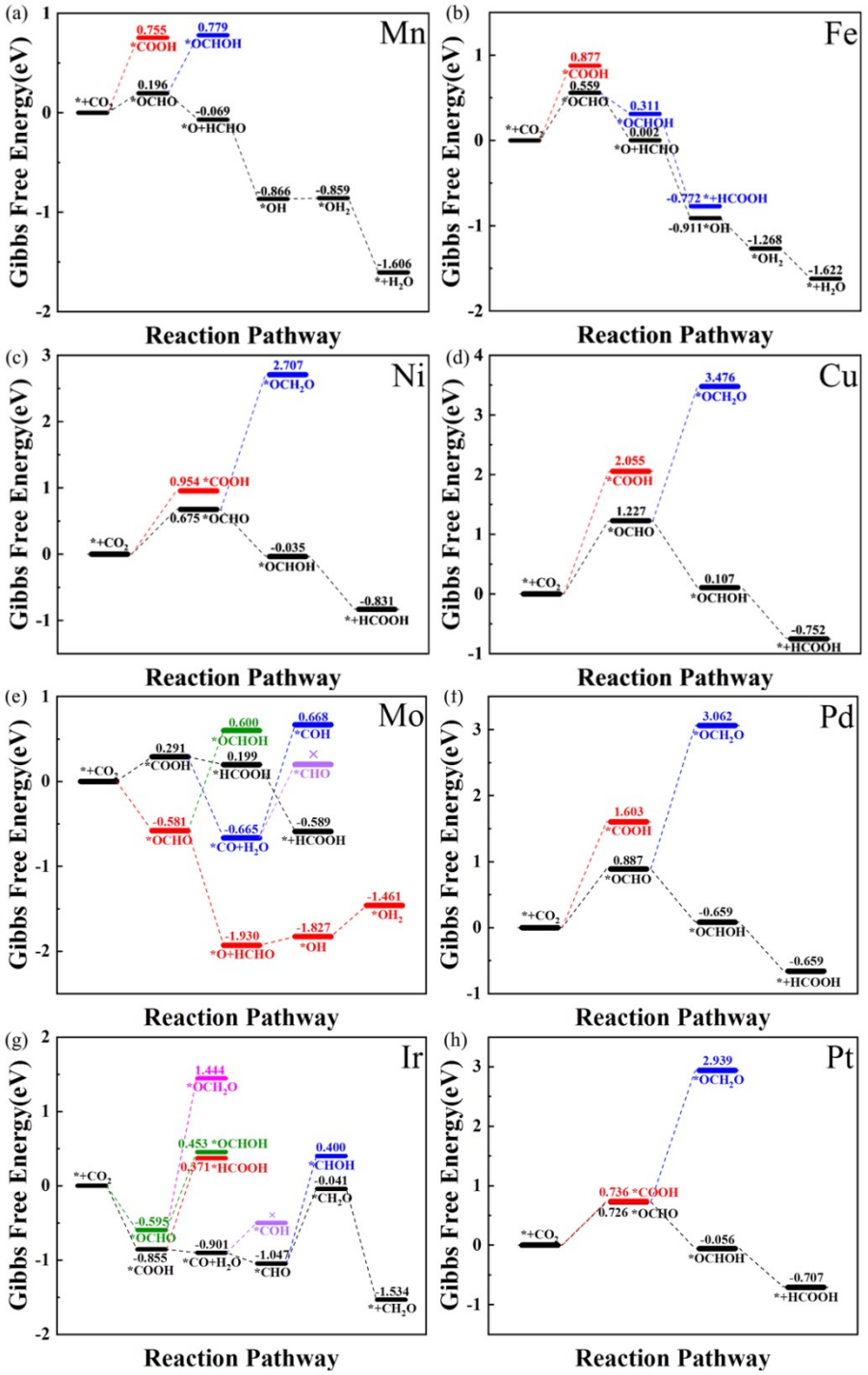

Fig. S6 Gibbs free energy profiles for CO_2RR on (a)MnClPP, (b)FeClPP, (c)NiClPP, (d)CuClPP, (e)MoClPP, (f)PdClPP, (g)IrClPP and (h)PtClPP at zero potential. The free energy zero is set as that of a CO_2 molecule in the gas phase and with a clean catalyst surface. The "X" in the profiles indicates that the intermediate is unstable. The black line is the most favorable pathway.

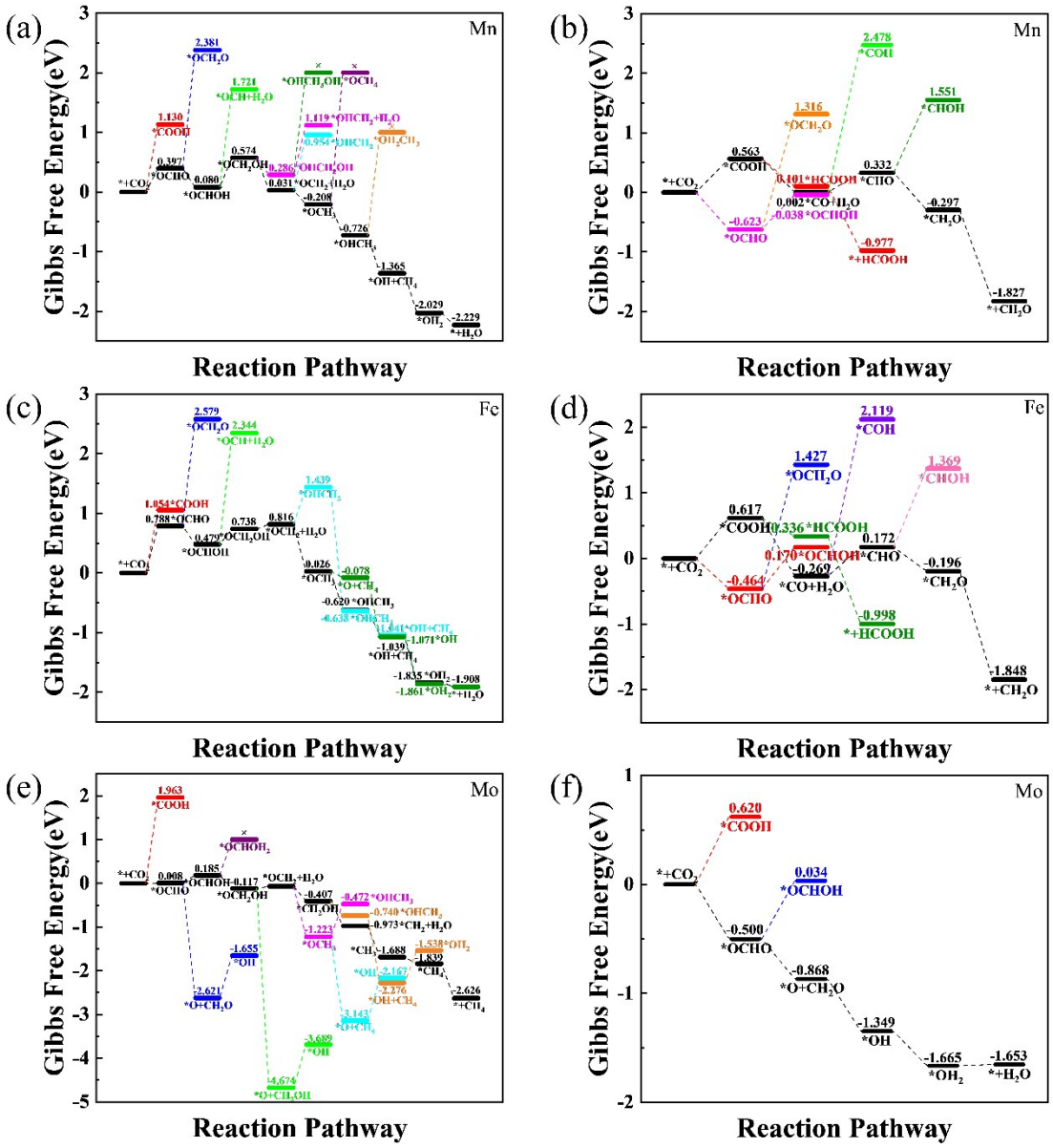

Fig. S7 Gibbs free energy profiles for CO_2RR on (a)MnNaPP, (b)MnSPP, (c)FeNaPP, (d)FeSPP, (e)MoNaPP and (f)MoSPP at zero potential. The free energy zero is set as that of a CO_2 molecule in the gas phase and with a clean catalyst surface. The "X" in the profiles indicates that the intermediate is unstable. The black line is the most favorable pathway.

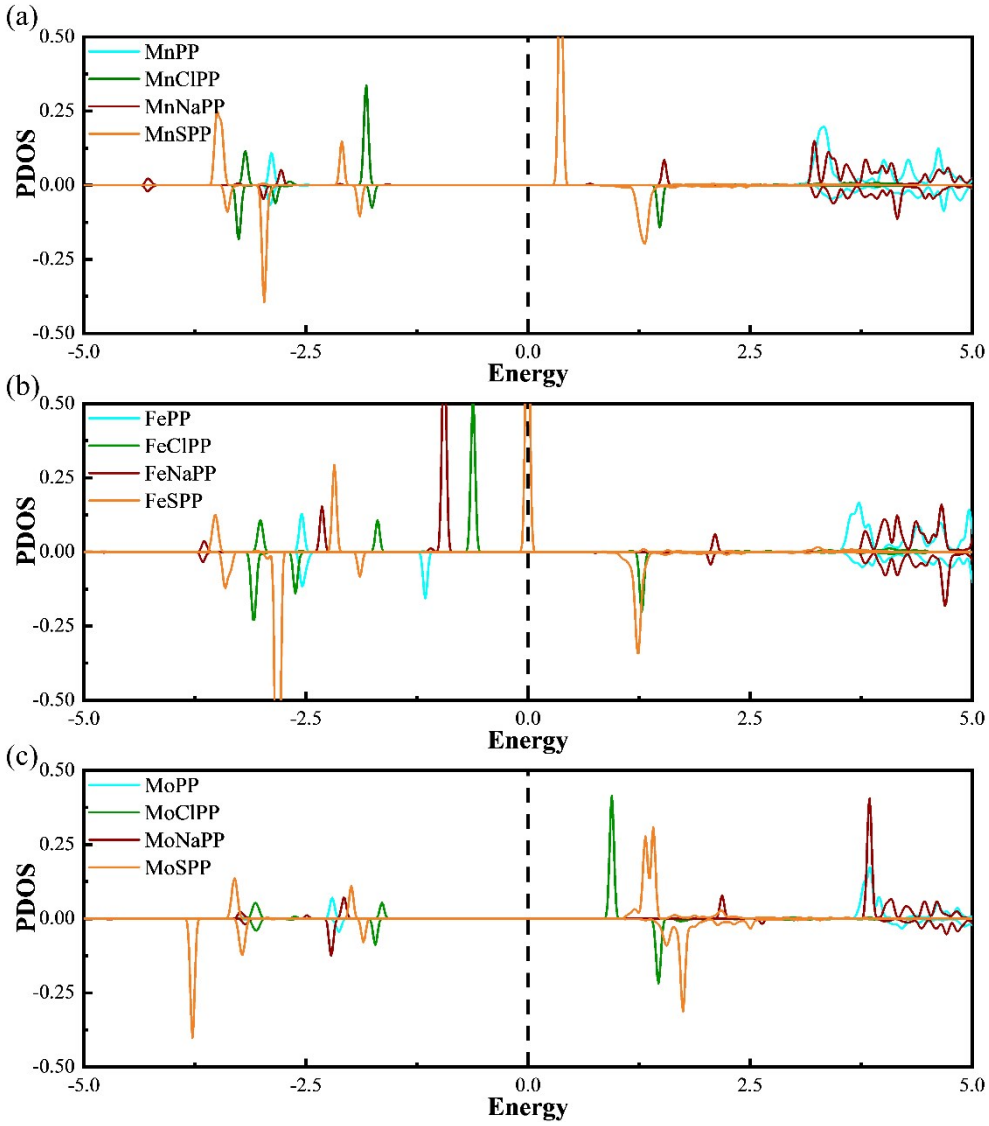

Fig. S8 PDOS of (a) Mn, (b)Fe and (c) Mo atoms when doped with different ions.

Table S1 Chemical potentials (μ) of gas-phase molecules obtained by summing up DFT electronic energy (E_{DFT}), zero-point energy (ZPE), enthalpic temperature correction ($\int C_P dT$), and entropy contribution (–TS). [a] Data from Lim et al[1]. [b] Data from Peterson et al[2]. [c] Data from the current study. All data are given in eV.

Species	E_{DFT}[c]	ZPE[a](ZPE[b])	$\int C_P dT$[b]	-TS[b]	μ(eV)
CH_4	–24.04	1.19(1.20)	0.10	–0.60	–23.34
CO_2	–22.95	0.28(0.31)	0.10	–0.65	–23.19
CO	–14.78	0.12(0.14)	0.09	–0.67	–15.22
CH_3OH	–30.22	(–1.35)	0.11	–0.79	–32.25
H_2	–6.77	0.3(0.27)	0.09	–0.42	–6.83
H_2O	–14.22	0.60(0.58)	0.10	–0.65	–14.19
HCOOH	–29.89	0.86(0.9)	0.11	–1.02	–29.90
CH_2O(HCHO)	–22.13	(–0.7)	0.10	–0.66	–23.39

Table S2 The electronic energy (E_{DFT}), zero point energy (ZPE), and entropy contribution (–TS) of adsorbate-surface systems on MPP, where M = Mn, Fe, Ni, Cu, Mo, Pd, Ir and Pt. The temperature of the reaction is 298.15 K. All data are given in eV.

Adsorbed species on MnPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–285.77841253	0.5844	–0.2000
*OCHOH	–289.59862081	0.9265	–0.2684
Adsorbed species on FePP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–284.02311661	0.5852	–0.2567
*OCHOH	–288.16335322	0.9220	–0.2832
Adsorbed species on NiPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–280.26407046	0.5616	–0.2072
*OCHOH	–285.32408735	0.9067	–0.2598
Adsorbed species on CuPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–277.80343014	0.5578	–0.2009
*OCHOH	–283.06709841	0.9098	–0.2605
Adsorbed species on MoPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–286.87843094	0.5942	–0.2585
*OCHOH	–289.91263921	0.9213	–0.2369
Adsorbed species on PdPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–279.95376489	0.5545	–0.2150
*OCHOH	–285.19776296	0.8933	–0.1683
Adsorbed species on IrPP	**E_{DFT}**	**ZPE**	**–TS**
*COOH	–284.95473398	0.6318	–0.1562
*HCOOH	–287.69480262	0.9010	–0.2258
Adsorbed species on PtPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–281.38644511	0.5612	–0.2772
*OCHOH	–286.66923170	0.8860	–0.2176

Table S3 The electronic energy (E_{DFT}), zero point energy (ZPE), and entropy contribution (–TS) of adsorbate-surface systems on MClPP, where M = Mn, Fe, Ni, Cu, Mo, Pd, Ir and Pt. All data are given in eV.

Adsorbed species on MnClPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–291.32625654	0.5629	–0.2384
*O+CH_2O	–271.30319921	0.0690	–0.0568
*OH	–275.75684294	0.3550	–0.1013
*OH_2	–279.41878353	0.6600	–0.1526
Adsorbed species on FeClPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–289.47395911	0.6025	–0.2213
*O+CH_2O/ *OCHOH	–269.69461495/ –293.51022311	0.0726/ 0.9494	–0.0528/ –0.1956
*OH	–274.24855348	0.3476	–0.1021
*OH_2	–278.30053476	0.6649	–0.1397
Adsorbed species on NiClPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–285.82529599	0.5734	–0.2589
*OCHOH	–290.21958811	0.8991	–0.3154
Adsorbed species on CuClPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–283.15555263	0.5629	–0.2700
*OCHOH	–288.03665625	0.8983	–0.2595
Adsorbed species on MoClPP	**E_{DFT}**	**ZPE**	**–TS**
*COOH	–292.36700416	0.6012	–0.1833
*HCOOH	–296.11854325	0.9091	–0.2471
Adsorbed species on PdClPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–285.44500083	0.5571	–0.2366
*OCHOH	–289.89936175	0.8794	–0.3248
Adsorbed species on IrClPP	**E_{DFT}**	**ZPE**	**–TS**
*COOH	–290.90362127	0.6230	–0.2156
*CO+H_2O	–279.87689838	0.2332	–0.1232
*CHO	–283.71194057	0.4795	–0.0951
*CH_2O	–286.24227416	0.7367	–0.2316
Adsorbed species on PtClPP	**E_{DFT}**	**ZPE**	**–TS**

*OCHO	–286.87146368	0.5684	–0.2655
*OCHOH	–291.37161234	0.8585	–0.2528

Table S4 The electronic energy (E_{DFT}), zero point energy (ZPE), and entropy contribution (–TS) of adsorbate-surface systems on MXPP, where M = Mn, Fe, and Mo, X= Na and S. All data are given in eV.

Adsorbed species on MnNaPP	**E_{DFT}**	**ZPE**	**-TS**
*OCHO	–283.88984085	0.5671	–0.1760
*OCHOH	–287.92208430	0.9223	–0.2309
*OCH_2OH	–291.06093975	1.2094	–0.2997
*OCH_2+H_2O	–280.44891277	0.7560	–0.2265
*OCH_3	–284.48901794	1.0589	–0.1436
*$OHCH_3$	–288.68945759	1.4078	–0.2252
*OH+CH_4	–268.42933007	0.3331	–0.1245
*OH_2	–272.74338160	0.6273	–0.1838
Adsorbed species on FeNaPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–282.19167177	0.5866	–0.2072
*OCHOH	–286.21364147	0.9360	–0.2583
*OCH_2OH	–289.59387388	1.2130	–0.3108
*OCH_2+H_2O	–278.38997146	0.7411	–0.1903
*OCH_3/ *$OHCH_2$	–282.91449711/ –281.36904487	1.0658/ 1.0244	–0.1951/ –0.2865
*$OHCH_3$/ *O+CH_4	–287.27666562/ –262.22797157	1.4076/ 0.0708	–0.2359/ –0.0655
*OH+CH_4/ *OH	–266.79131062/ –266.80629702/	0.3229/ 0.3193	–0.1309/ –0.1441
*OH_2	–271.23867018/ –271.27248648	0.6373/ 0.6408	–0.2086/ –0.2040
Adsorbed species on MoNaPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–284.54706632	0.5935	–0.2561
*OCHOH	–288.13830475	0.9322	–0.2419

*OCH_2OH	–292.20610086	1.2364	–0.1954
*OCH_2+H_2O	–280.92708700	0.7510	–0.1645
*CH_2OH	–284.95984391	1.0840	–0.2193
*CH_2+H_2O	–274.35528727	0.5956	–0.1265
*CH_3	–278.81717133	0.9190	–0.1181
*CH_4	–282.59337561	1.2017	–0.1905
Adsorbed species on MnSPP	**E_{DFT}**	**ZPE**	**–TS**
*COOH	–292.20720968	0.6130	–0.1747
*CO+H_2O/ *HCOOH	–281.61095461/ –296.30127078	0.1984/ 0.8979	–0.1418/ –0.2419
*CHO	–284.90417098	0.4402	–0.1757
*CH_2O	–289.08759458	0.7178	–0.3134
Adsorbed species on FeSPP	**E_{DFT}**	**ZPE**	**–TS**
*COOH	–290.68597416	0.6152	–0.1856
*CO+H_2O/ *HCOOH	–280.44180630/ –294.68130917	0.2115/ 0.8992	–0.1375/ –0.1704
*CHO	–283.63400729	0.4528	–0.1602
*CH_2O	–287.61056082	0.7358	–0.2504
Adsorbed species on MoSPP	**E_{DFT}**	**ZPE**	**–TS**
*OCHO	–295.42469752	0.5621	–0.2224
*O+CH_2O	–275.48105776	0.0663	–0.0632
*OH	–279.58353434	0.3287	–0.1190
*OH_2	–283.51458385	0.6281	–0.2186

Table S5 The energy of the catalyst to adsorb HCOOH, CO, CH_2O, CH_3OH and CH_4 on MPP, where M = Mn, Fe, Ni, Cu, Mo, Pd, Ir and Pt. All data are given in eV.

Catalyst	HCOOH	CO	CH_2O
Mn	–0.552	/	/
Fe	–0.494	/	/
Ni	–0.293	/	/
Cu	–0.343	/	/
Mo	–0.664	-3.386	-0.232
Pd	–0.260	/	/
Ir	–0.618	-1.457	-0.503
Pt	–0.334	/	/

Table S6 Equilibrium potentials of several possible CO_2RR cathode reactions[3].

Reactions	Uequ vs RHE(V)
$CO_2+2H^++2e^-\rightarrow CO(g)+H_2O$	–0.12
$CO_2+2H^++2e^-\rightarrow HCOOH(l)$	–0.20
$CO_2+4H^++4e^-\rightarrow HCHO(l)+H_2O$	–0.07
$CO_2+6H^++6e^-\rightarrow CH_3OH(l)+H_2O$	0.03
$CO_2+8H^++8e^-\rightarrow CH_4(g)+2H_2O$	0.17

Table S7 The potential determining steps (PDS), maximum free energy change (ΔG_{max}/eV), reduction products and overpotentials (η/V) of the CO_2RR on MPP, where M = Mn, Fe, Ni, Cu, Mo, Pd, Ir and Pt.

Catalyst	PDS	ΔG_{max} (eV)	Product	η (V)
Mn	$*CO_2\rightarrow *OCHO$	0.228	HCOOH	0.028
Fe	$*CO_2\rightarrow *OCHO$	0.471	HCOOH	0.271
Ni	$*CO_2\rightarrow *OCHO$	1.604	HCOOH	1.404
Cu	$*CO_2\rightarrow *OCHO$	1.782	HCOOH	1.582
Mo	$*OCHO\rightarrow *OCHOH$	0.729	HCOOH	0.529
Pd	$*CO_2\rightarrow *OCHO$	1.830	HCOOH	1.630
Ir	$*COOH\rightarrow *HCOOH$	0.875	HCOOH	0.675
Pt	$*CO_2\rightarrow *OCHO$	1.764	HCOOH	1.564

Table S8 The potential determining steps (PDS), maximum free energy change (ΔG_{max}/eV), reduction products and overpotentials (η/V) of the CO_2RR on MClPP, where M = Mn, Fe, Ni, Cu, Mo, Pd, Ir and Pt.

Catalyst	PDS	ΔG_{max} (eV)	Product	η (V)
Mn	$*CO_2 \rightarrow *OCHO$	0.196	HCHO	0.126
Fe	$*CO_2 \rightarrow *OCHO$	0.559	HCHO/HCOOH	0.489/0.359
Ni	$*CO_2 \rightarrow *OCHO$	0.675	HCOOH	0.475
Cu	$*CO_2 \rightarrow *OCHO$	1.227	HCOOH	1.027
Mo	$*CO_2 \rightarrow *COOH$	0.291	HCOOH	0.091
Pd	$*CO_2 \rightarrow *OCHO$	0.887	HCOOH	0.687
Ir	$*CHO \rightarrow *CH_2O$	1.005	HCHO	0.935
Pt	$*CO_2 \rightarrow *OCHO$	0.726	HCOOH	0.526

Table S9 The potential determining steps (PDS), maximum free energy change (ΔG_{max}/eV), reduction products and overpotentials (η/V) of the CO_2RR on MXPP, where M = Mn, Fe, and Mo, X= Na and S.

Catalyst	PDS	ΔG_{max} (eV)	Product	η (V)
Mn (Na^+)	$*OCHOH \rightarrow *OCH_2OH$	0.494	CH_4	0.663
Mn (S^{2-})	$*CO_2 \rightarrow *COOH$	0.563	HCHO/HCOOH	0.493/0.313
Fe (Na^+)	$*CO_2 \rightarrow *OCHO$	0.788	CH_4	0.957
Fe (S^{2-})	$*CO_2 \rightarrow *COOH$	0.617	HCHO/HCOOH	0.547/0.367
Mo (Na^+)	$*OCHO \rightarrow *OCHOH$	0.177	CH_4	0.346
Mo (S^{2-})	$*OH_2 \rightarrow * + H_2O$	0.012	HCHO	-0.060

References

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2. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. R. Osmiumsl and J. K. Nerskov, *Energ. Environ. Sci.*, 2010, **3**, 1311-1315.
3. C. Oloman and H. Li, *ChemSusChem*, 2008, **1**, 385-391.