Supplementary Information

Towards Efficient CO_2RR Electrocatalysts: A Study of Structure and Properties of M–N–E Active Moieties Embedded in Biphenylene Framework (M = Mn, Fe, Co, Ni, Cu; E = C, B)

Zhengqin Zhao,[a] Andrey V. Zibarev,[b] Hui Wang,[a,*] Jinbo Hao[c] and Lijia Luo[a]

[a] *School of Physical Science and Technology, Southwest Jiaotong University, Chengdu 610031, P. R. China. E-mail: wanghui@swjtu.edu.cn (H. Wang)*

[b] *Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russia*

[c] *School of Science, Xi'an University of Architecture and Technology, Xi'an 710055, Shaanxi, China*

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1. Figures

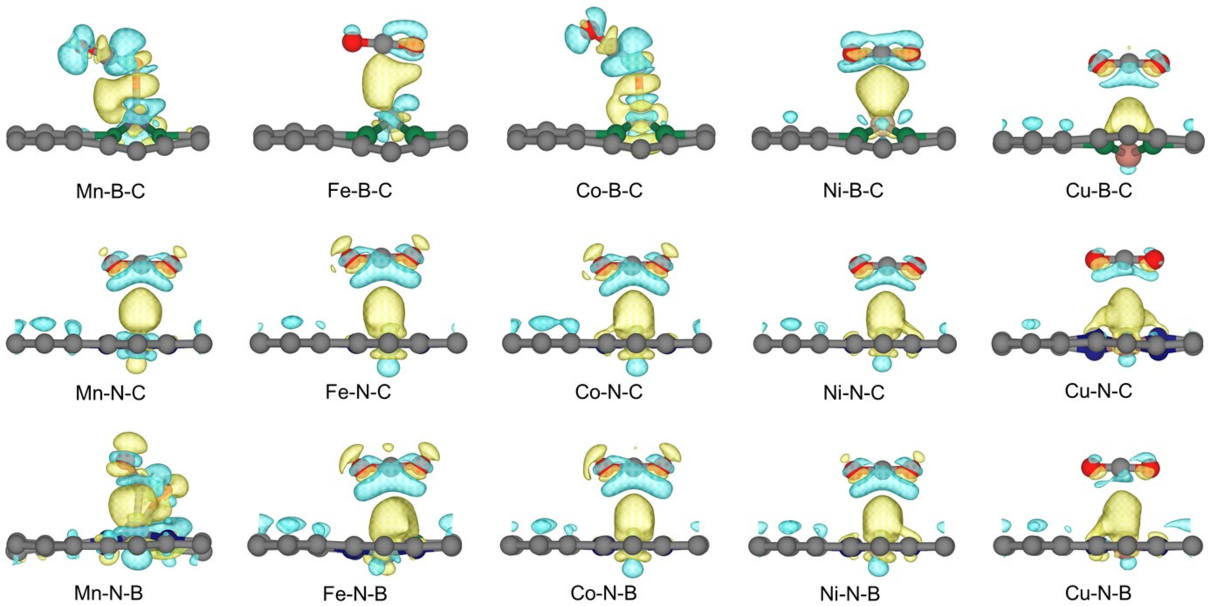


Figure S1. The differential charge density diagram of CO_2 adsorbed at the M–B–C-, M–N–C-, and M–N–B-modified BPN monolayers (M = Mn, Fe, Co, Ni, Cu). Color code: yellow, charge accumulation; cyan, charge depletion. The isosurface ρ = 0.00025 e $Bohr^{-3}$.

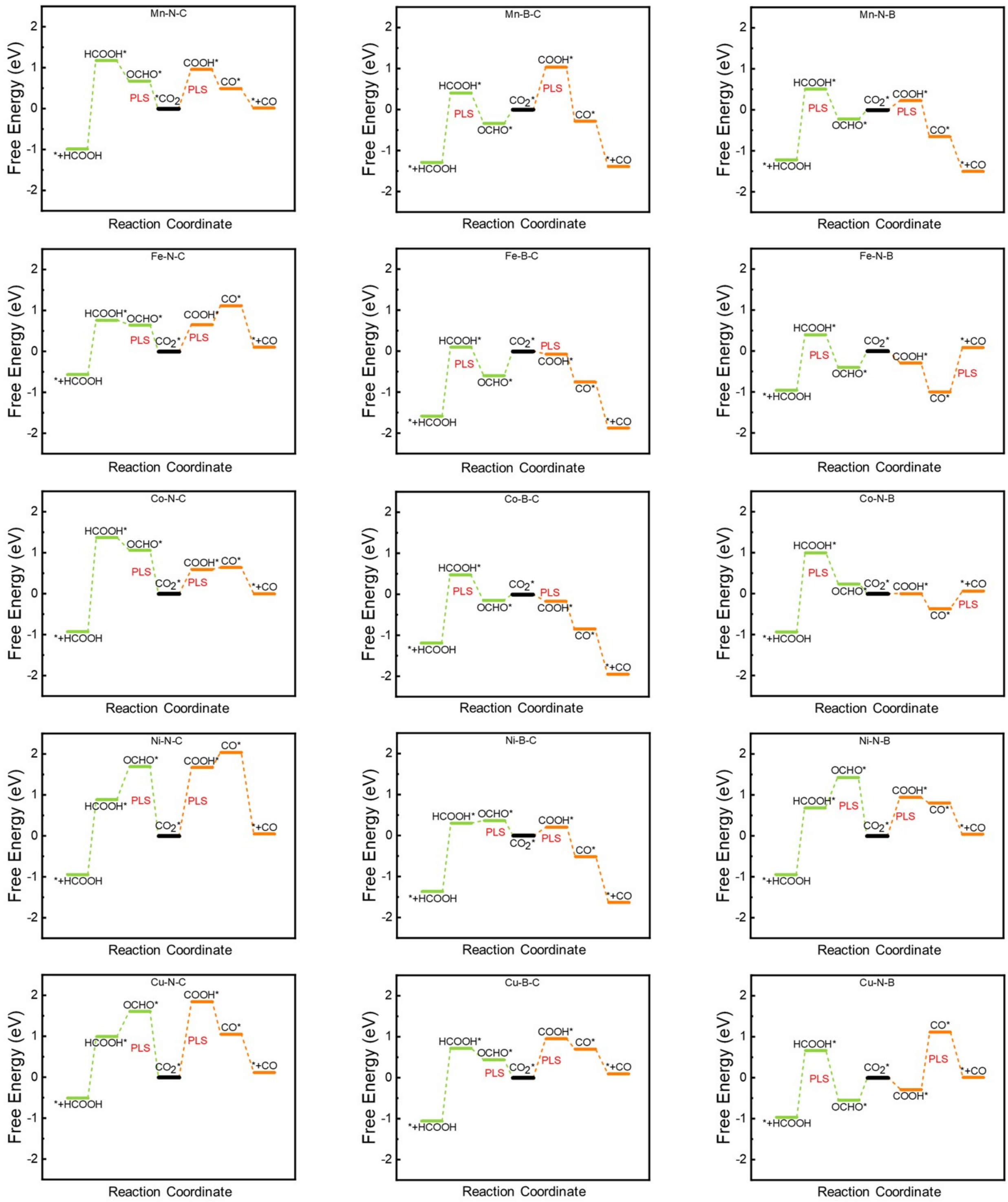


Figure S2. The free energy diagrams of two-electron reaction coordinate for the M–B–C, M–N–C, and M–N–B active moieties.

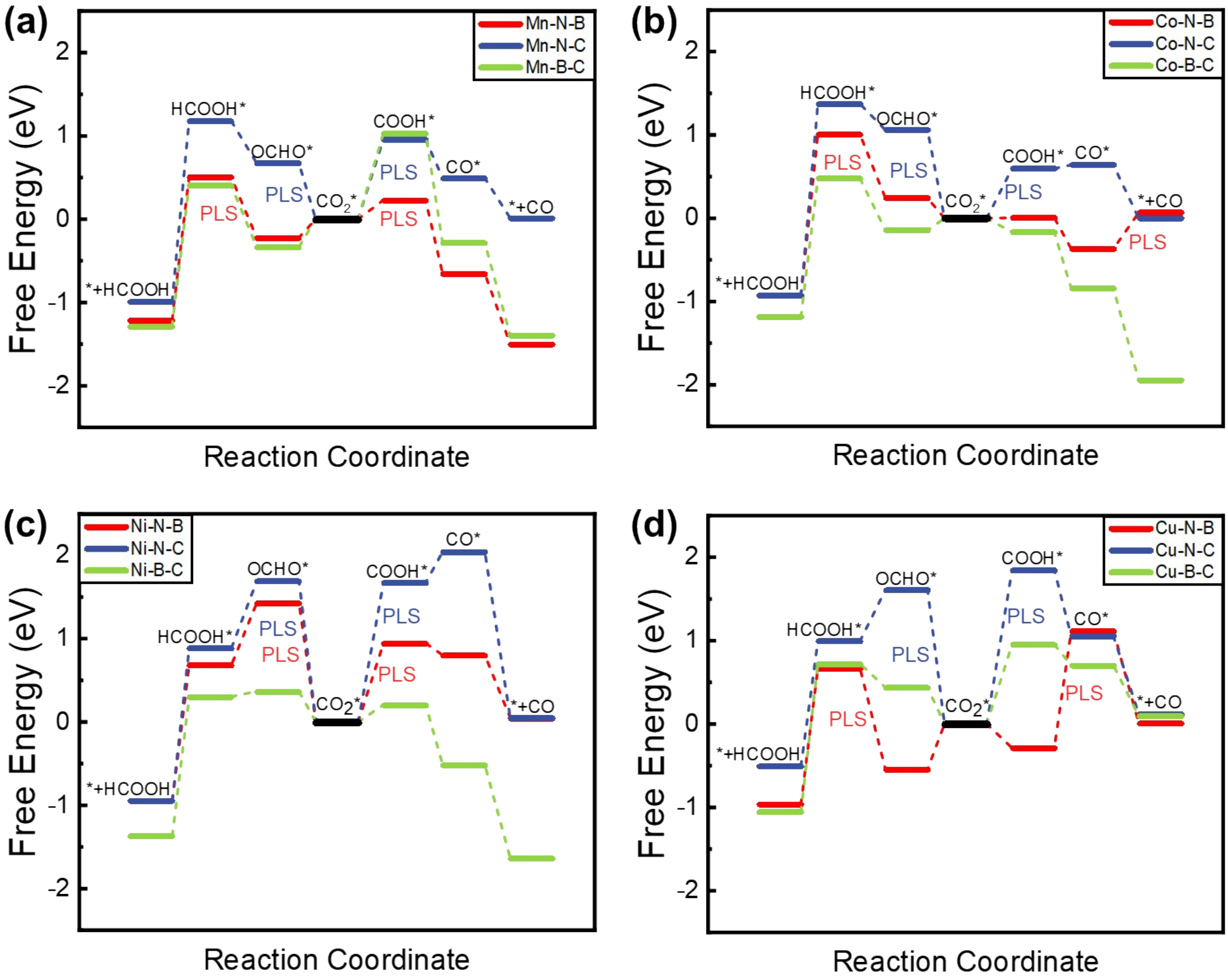


Figure S3. The free energy diagrams for the two-electron reaction coordinate for various active moieties with M = Mn, Co, Ni, and Cu.

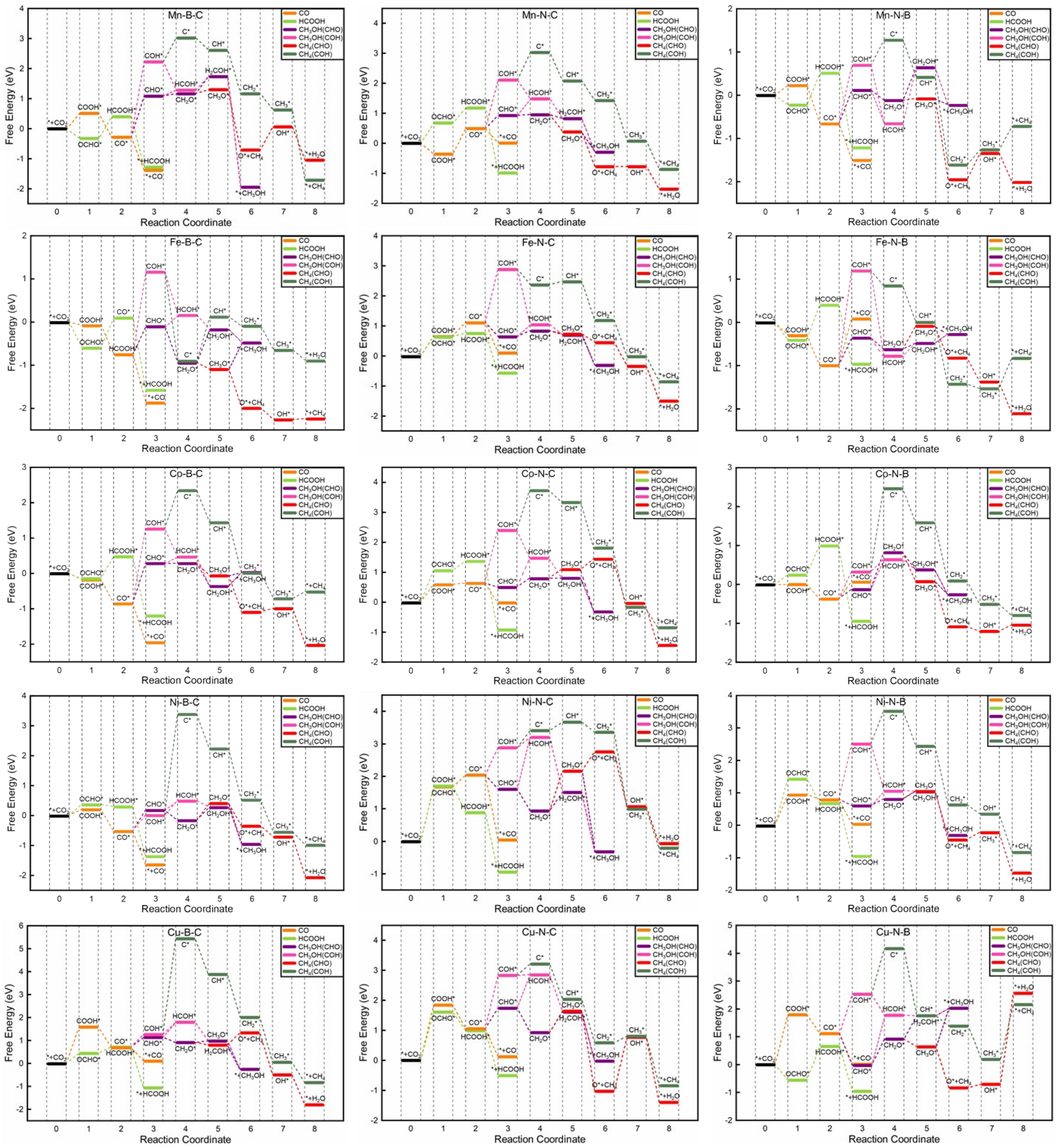


Figure S4. The free energy diagrams of the CO_2RR reaction coordinate for the M–B–C, M–N–C and M–N–B (M = Mn, Fe, Co, Ni, Cu) active moieties.

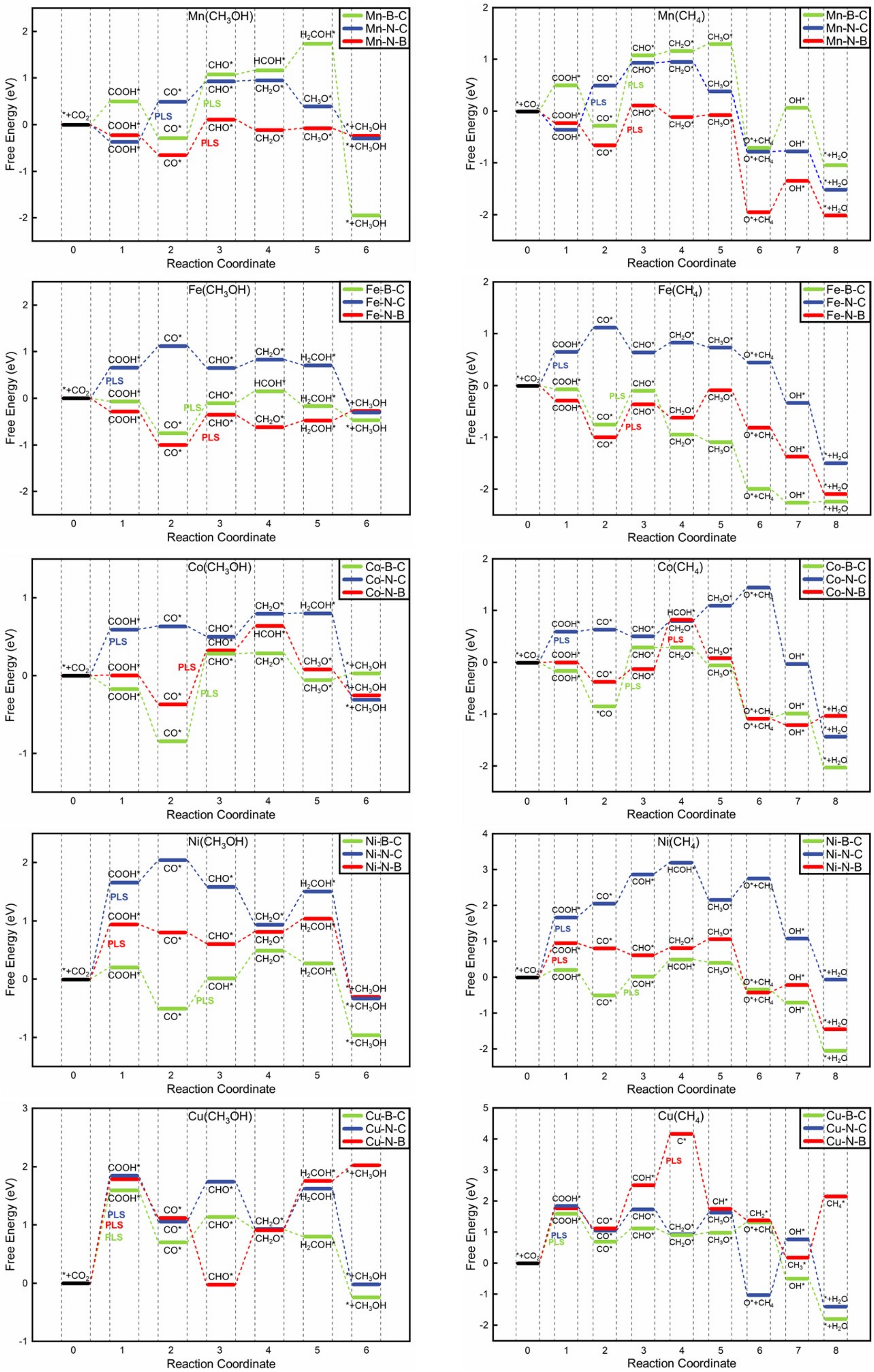


Figure S5. Optimal reaction coordinates for the production of CH_3OH and CH_4 from metal center atoms M (M = Mn, Fe, Co, Ni, and Cu) with different coordination environments.

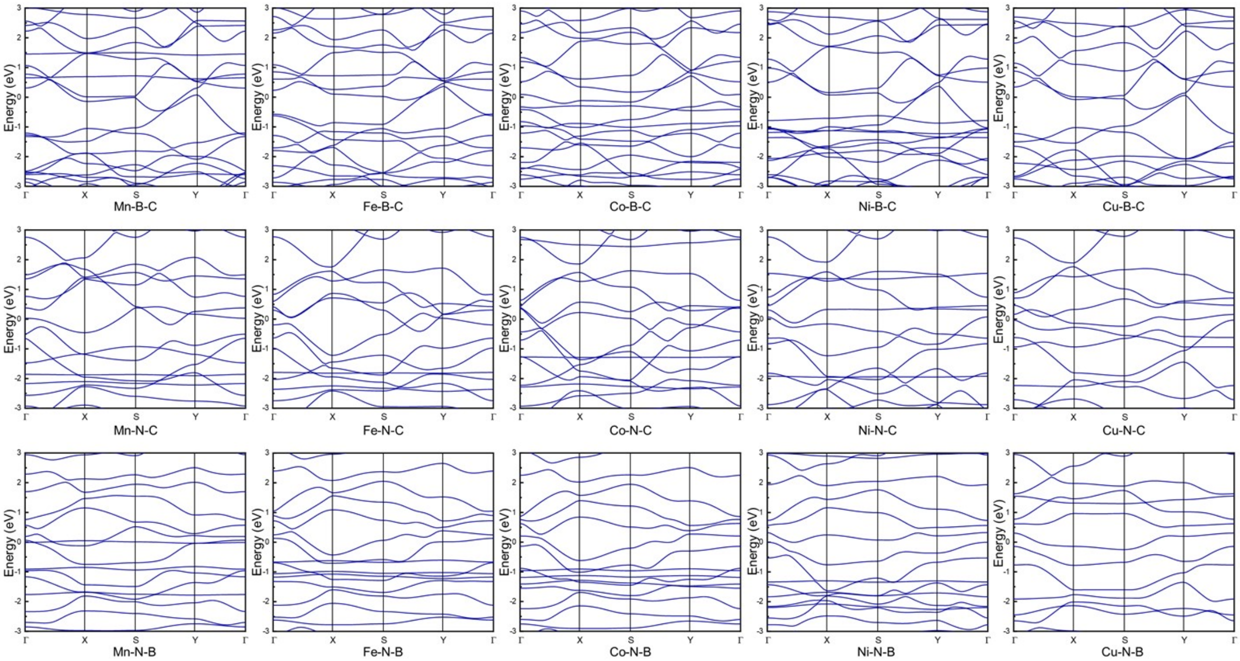


Figure S6. The solid-state electron-energy band diagrams for the M–B–C, M–N–C, and M–N–B-modified BPN monolayers.

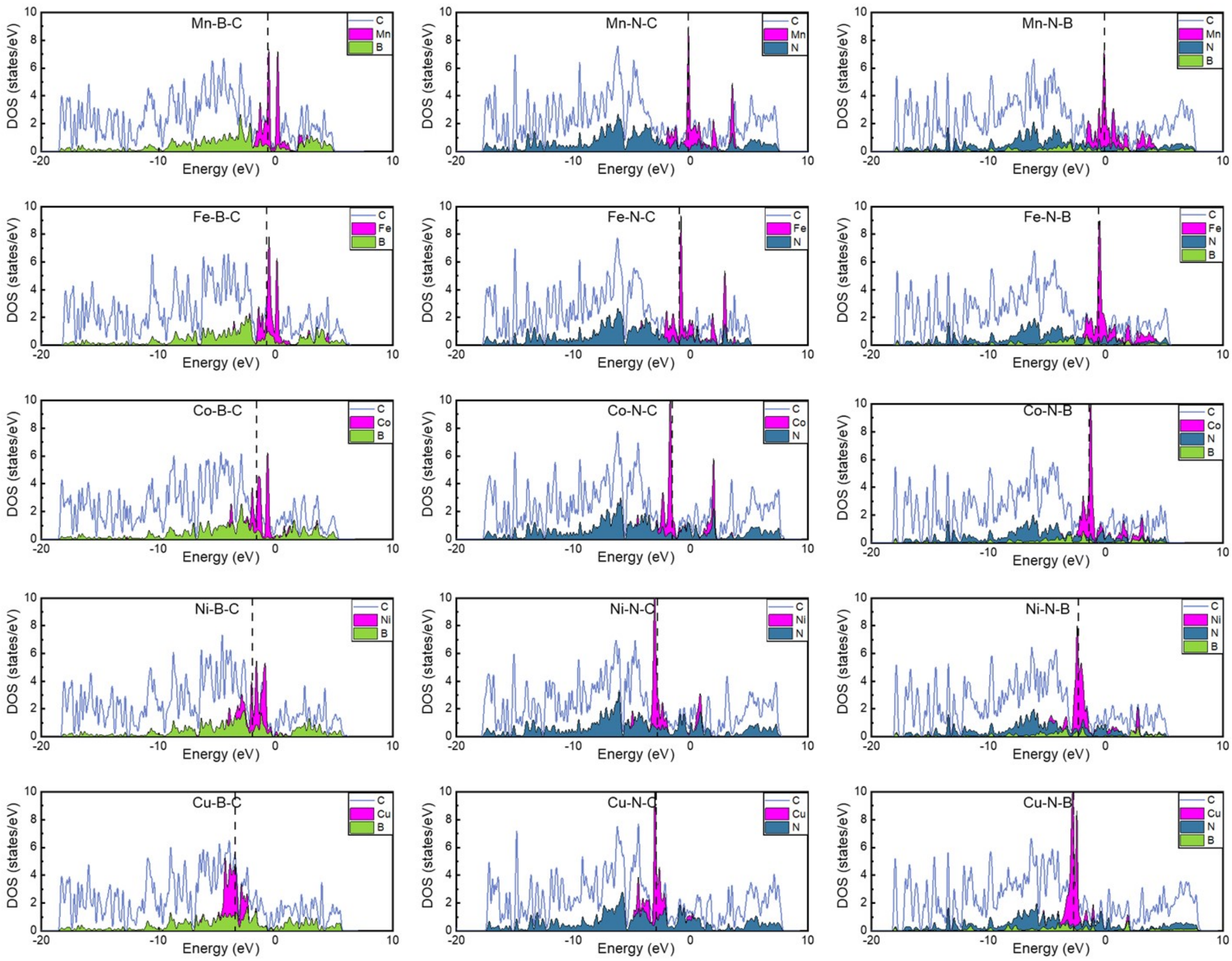


Figure S7. The projected DOS of the M–B–C, M–N–C, and M–N–B active moieties featuring the centers of electric-energy bands originated from d-AOs of the M atoms marked by vertical dotted lines.

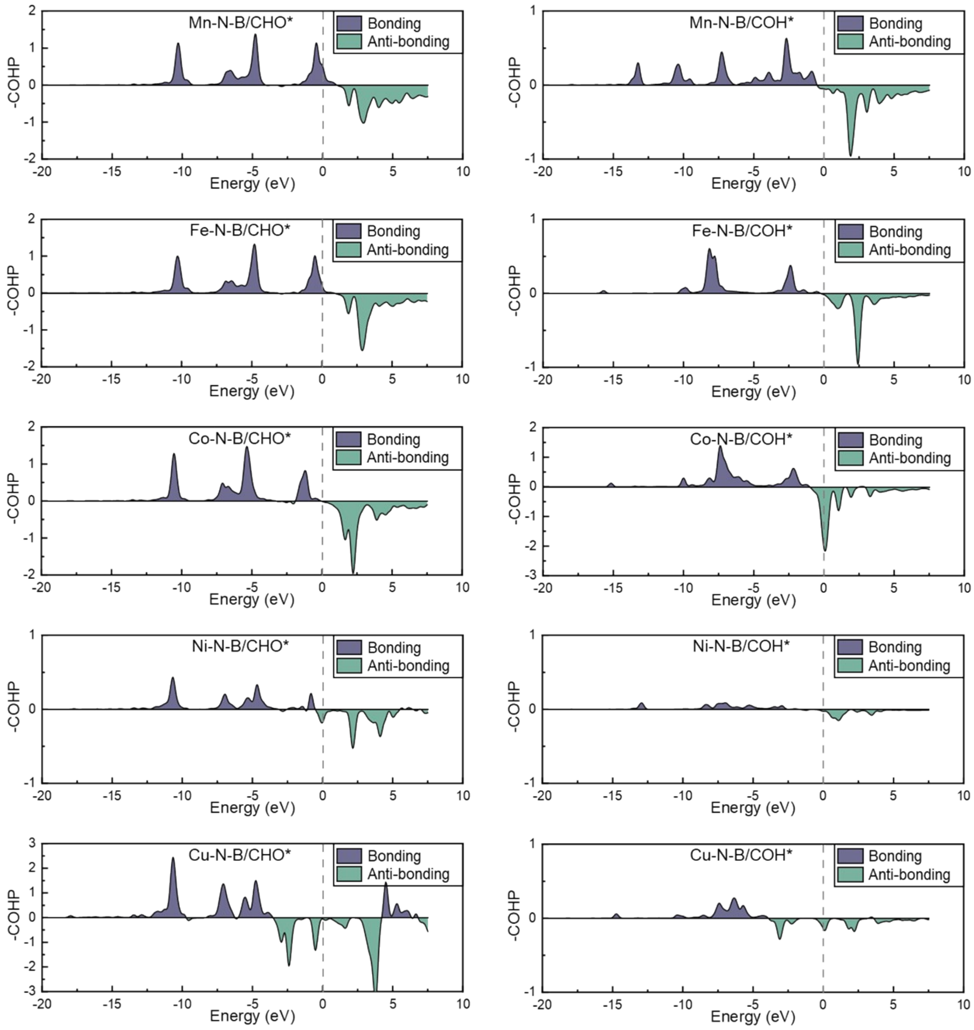


Figure S8. The COHP diagrams for the M–N–B active moieties with adsorbed CHO* and COH*. Color code: purple, bonding states; green, antibonding states.

2. Tables

Table S1. Calculated energy, zero-point energy correction, enthalpy correction, and entropy contribution of free molecules, eV.

Species	E	ZPE	$\int C_p dT$	TS
CO_2	-23.31	0.31	0.10	0.66
CO	-15.26	0.13	0.09	0.61
HCOOH	-29.71	0.88	0.11	0.86
CH_3OH	-29.75	1.39	0.11	0.82
CH_4	-23.45	1.20	0.10	0.60
H_2O	-14.33	0.57	0.10	0.67
H_2	-6.91	0.27	0.09	0.40

Table S2. Calculated energy, zero-point energy correction, enthalpy correction, and entropy contribution of adsorbed molecules, eV.

Species	ZPE	$\int C_p dT$	TS
COOH	0.62	0.11	0.22
OCHO	0.69	0.10	0.21
CO	0.13	0.09	0.61
HCOOH	0.98	0.11	0.16
CHO	0.48	0.08	0.16
COH	0.48	0.05	0.05
C	0.08	0.07	0.03
CH_2O	0.76	0.10	0.22
HCOH	0.79	0.08	0.13
CH	0.35	0.04	0.07
CH_2OH	1.12	0.08	0.19
CH_3O	1.10	0.11	0.18
CH_2	0.63	0.06	0.09
CH_3	0.96	0.07	0.08
OH	0.36	0.05	0.08

Table S3. The potential limiting step and corresponding limiting potential U_L (V) of the CO_2RR on the M–N–C, M–B–C, and M–N–B active moieties [a].

Active moiety	Products	PLS	U_L
Mn–N–C	CO	$COOH^* + H^+ + e^- \rightarrow CO^*$	–0.85
	HCOOH	$CO_2 + * + H^+ + e^- \rightarrow OHCO^*$	–0.67
	CH_3OH	$COOH^* + H^+ + e^- \rightarrow CO^*$	–0.85
	CH_4	$COOH^* + H^+ + e^- \rightarrow CO^*$	–0.85
Fe–N–C	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.66
	HCOOH	$CO_2 + * + H^+ + e^- \rightarrow OHCO^*$	–0.65
	CH_3OH	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.66
	CH_4	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.66
Co–N–C	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.60
	HCOOH	$CO_2 + * + H^+ + e^- \rightarrow OHCO^*$	–1.06
	CH_3OH	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.60
	CH_4	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.60
Ni–N–C	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.67
	HCOOH	$CO_2 + * + H^+ + e^- \rightarrow OHCO^*$	–1.69
	CH_3OH	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.67
	CH_4	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.67
Cu–N–C	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.85
	HCOOH	$CO_2 + * + H^+ + e^- \rightarrow OHCO^*$	–1.61
	CH_3OH	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.85
	CH_4	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.85
Mn-B-C	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.50
	HCOOH	$OHCO^* + H^+ + e^- \rightarrow HCOOH^*$	–0.74
	CH_3OH	$CO^* + H^+ + e^- \rightarrow CHO^*$	–1.37
	CH_4	$CO^* + H^+ + e^- \rightarrow CHO^*$	–1.37
Fe–B–C	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	0.07
	HCOOH	$OHCO^* + H^+ + e^- \rightarrow HCOOH^*$	–0.69
	CH_3OH	$CH_2O^* + H^+ + e^- \rightarrow CH_2OH^*$	–0.77
	CH_4	$CO^* + H^+ + e^- \rightarrow CHO^*$	–0.65
Co–B–C	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	0.17
	HCOOH	$OHCO^* + H^+ + e^- \rightarrow HCOOH^*$	–0.62
	CH_3OH	$CO^* + H^+ + e^- \rightarrow CHO^*$	–1.13

	CH_4	$CO^* + H^+ + e^- \rightarrow CHO^*$	–1.13
Ni–B–C	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.21
	HCOOH	$CO_2 + * + H^+ + e^- \rightarrow OHCO^*$	–0.37
	CH_3OH	$CO^* + H^+ + e^- \rightarrow CHO^*$	–0.69
	CH_4	$CO^* + H^+ + e^- \rightarrow CHO^*$	–0.69
Cu–B–C	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.60
	HCOOH	$CO_2 + * + H^+ + e^- \rightarrow OHCO^*$	–0.44
	CH_3OH	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.60
	CH_4	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.60
Mn-N-B	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	0.23
	HCOOH	$OHCO^* + H^+ + e^- \rightarrow HCOOH^*$	–0.73
	CH_3OH	$CO^* + H^+ + e^- \rightarrow CHO^*$	–0.77
	CH_4	$CO^* + H^+ + e^- \rightarrow CHO^*$	–0.77
Fe–N–B	CO	$CO^* \rightarrow CO + *$	–1.08
	HCOOH	$OHCO^* + H^+ + e^- \rightarrow HCOOH^*$	–0.80
	CH_3OH	$CO^* + H^+ + e^- \rightarrow CHO^*$	–0.63
	CH_4	$CO^* + H^+ + e^- \rightarrow CHO^*$	–0.63
Co–N–B	CO	$CO^* \rightarrow CO + *$	–0.44
	HCOOH	$OHCO^* + H^+ + e^- \rightarrow HCOOH^*$	–0.76
	CH_3OH	$CO^* + H^+ + e^- \rightarrow COH^*$	–0.69
	CH_4	$CHO^* + H^+ + e^- \rightarrow CH_2O^*$	–0.94
Ni–N–B	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.95
	HCOOH	$CO_2 + * + H^+ + e^- \rightarrow OHCO^*$	–1.43
	CH_3OH	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.95
	CH_4	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–0.95
Cu–N–B	CO	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.79
	HCOOH	$OHCO^* + H^+ + e^- \rightarrow HCOOH^*$	–1.21
	CH_3OH	$CO_2 + * + H^+ + e^- \rightarrow COOH^*$	–1.79
	CH_4	$COH^* + H^+ + e^- \rightarrow C^*$	–1.97

[a] Symbol * denotes adsorption / adsorbed state.

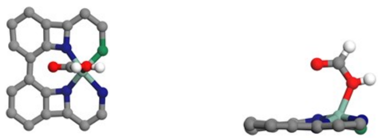
Table S4. Bader charges and CTs in the M–N–E-modified BPN frameworks, e.

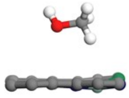
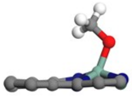
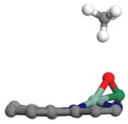
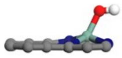
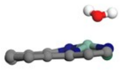
Triad	M	Bader charge	Original charge	Bader CT difference
M–B–C	Mn	12.43	13	-0.57
	Fe	7.70	8	-0.30
	Co	8.97	9	-0.03
	Ni	10.08	10	0.08
	Cu	10.92	11	-0.08
M–N–C	Mn	11.78	13	-1.22
	Fe	7.00	8	-1.00
	Co	8.05	9	-0.95
	Ni	9.10	10	-0.90
	Cu	10.06	11	-0.94
M–N–B	Mn	11.93	13	-1.07
	Fe	7.24	8	-0.76
	Co	8.42	9	-0.58
	Ni	9.46	10	-0.54
	Cu	10.34	11	-0.66

Table S5. The bonding energy for hydrogen adsorption of various active moieties in M–B–C, M–N–C and M–N–B (M= Mn, Fe, Co, Ni, Cu), eV.

	M–B–C	M–N–C	M–N–B
Mn	-4.83	-2.08	-0.97
Fe	-4.11	-3.79	-0.97
Co	-2.80	-2.14	-0.51
Ni	-2.03	-0.19	0.58
Cu	-1.57	2.08	0.59

Table S6. The optimized configurations and Gibbs free energy ΔG (eV) of reactants and intermediates adsorbed at the Fe–N–B active site, as well as the SBIs lengths between intermediates and B (Å) [a].

Reactants / intermediates		Optimized configurations	ΔG	SBIs
	COOH*		–0.28	1.93
CO	CO*		–0.99	2.11
	*+CO		0.09	-
	OCHO*		–0.40	1.45
HCOOH	HCOOH*		0.40	2.67
	*+HCOOH		–0.95	-
	CHO*		–0.36	1.91
CH_3OH	CH_2O*		–0.61	1.80
	CH_2OH*		–0.48	1.76

	*+CH_3OH			–0.27	-
CH_4	OCH_3			–0.08	2.65
	O*+CH_4			–0.81	1.34
	OH*			–1.37	2.44
	*+H_2O			–2.10	-

[a] Color code: C gray, H white, B green, N blue, O red, Fe cyan.