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First-row transition metal embedded pyrazine-based graphynes as high-performance single atom catalysts for CO_2 reduction reaction

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Table S1. Comparison of structural parameters (unit of Å) in this work and previous results.

	Lattice constant (a = b)	C–C-1	C–C-2	C–C-3	C–N
This work	6.76	1.44	1.41	1.22	1.34
Ref. [1]	6.76	1.44	1.41	1.22	1.34

Table S2. The binding energies (in eV) of the TM atoms on different sites of pyGY. Mn atom on site 3 and Zn atom on site 2 move to site 1 after optimization.

	Site 1	Site 2	Site 3
Sc-pyGY	5.26	5.11	3.41
Ti-pyGY	4.54	5.48	3.58
V-pyGY	4.29	4.62	2.62
Cr-pyGY	3.55	3.13	0.60
Mn-pyGY	3.50	3.09	–
Fe-pyGY	3.77	3.28	1.43
Co-pyGY	4.04	3.83	1.48
Ni-pyGY	4.72	4.54	1.81
Cu-pyGY	3.71	2.69	0.17
Zn-pyGY	0.79	–	0.14

Table S3. The formation energy E_f, bond lengths of M–C/N, cohesive energy E_{coh}, and Bader charge of the TM atom of TM-pyGYs.

	E_f (eV)	M–C/N (Å)	E_{coh} (eV/atom)	Charge (|e|)
Sc-pyGY	-0.86	2.09	6.78	-1.56
Ti-pyGY	0.34	2.10	6.78	-1.18
V-pyGY	1.23	2.05	6.76	-1.05
Cr-pyGY	0.86	2.04	6.73	-0.80
Mn-pyGY	0.75	1.99	6.73	-0.98
Fe-pyGY	1.48	1.95	6.74	-0.90
Co-pyGY	1.49	1.91	6.75	-0.66
Ni-pyGY	0.90	1.87	6.76	-0.43
Cu-pyGY	0.14	1.91	6.74	-0.50
Zn-pyGY	0.35	1.91	6.67	-0.96

Table S4. The adsorption energies (in eV) of CO_2 and H atom on TM-pyGYs.

	CO_2	H atom
Ti-pyGY	-0.36	-0.30
V-pyGY	-0.75	-0.09
Cr-pyGY	-0.23	0.40
Mn-pyGY	-0.25	0.31
Fe-pyGY	-0.30	0.11
Co-pyGY	-0.31	0.02
Ni-pyGY	-0.27	0.25
Cu-pyGY	-0.24	1.83

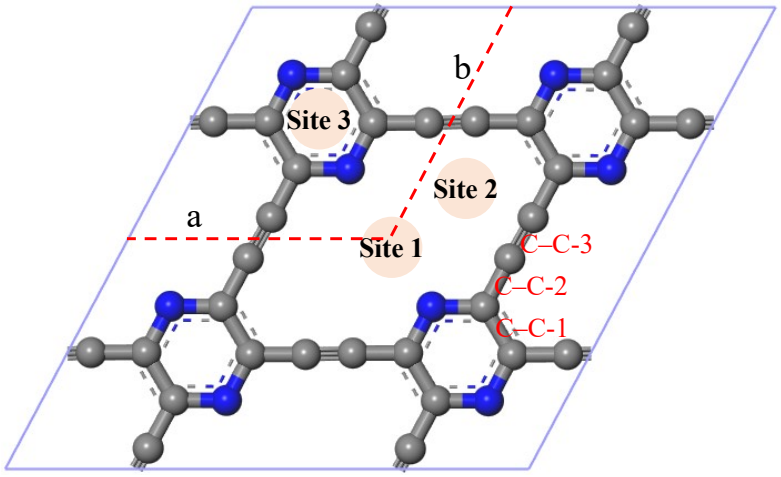

Fig. S1. A (2 × 2) supercell of pyGY. The unit cell is indicated by the red dashed line.

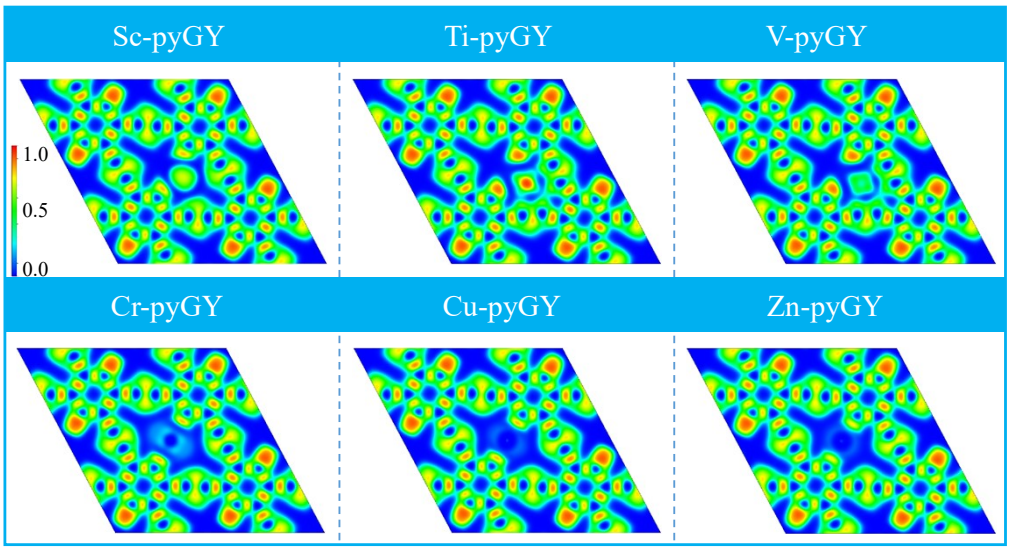

Fig. S2. ELF of TM-pyGYs.

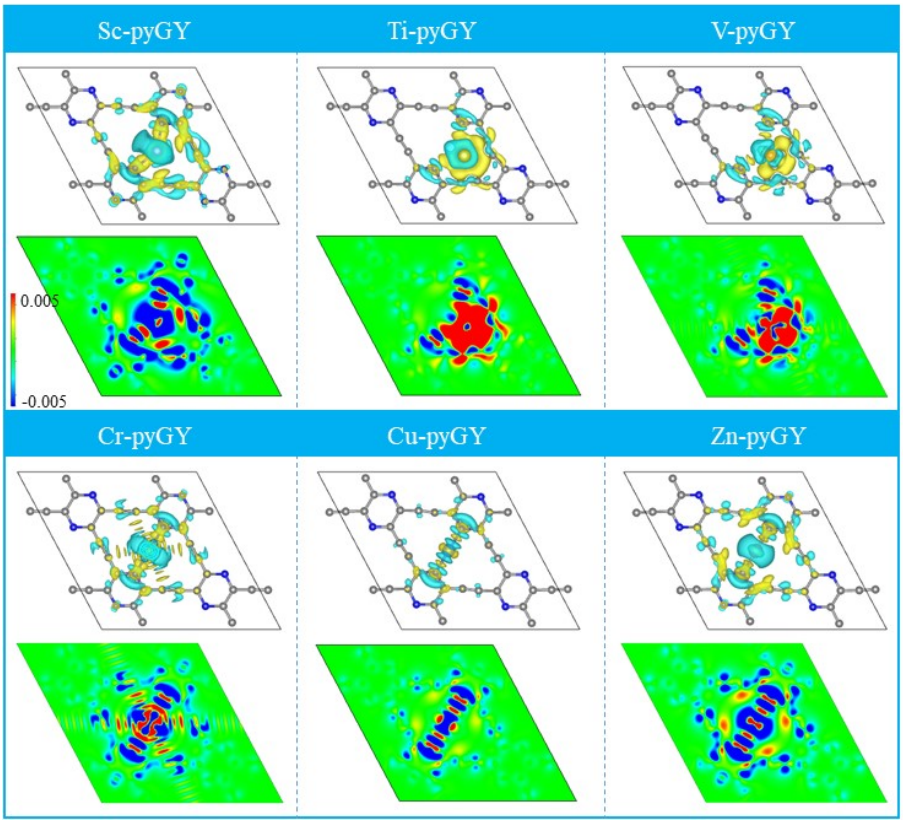

Fig. S3. Charge density difference of TM-pyGYs. The values of isosurface are 0.003 e/Å.

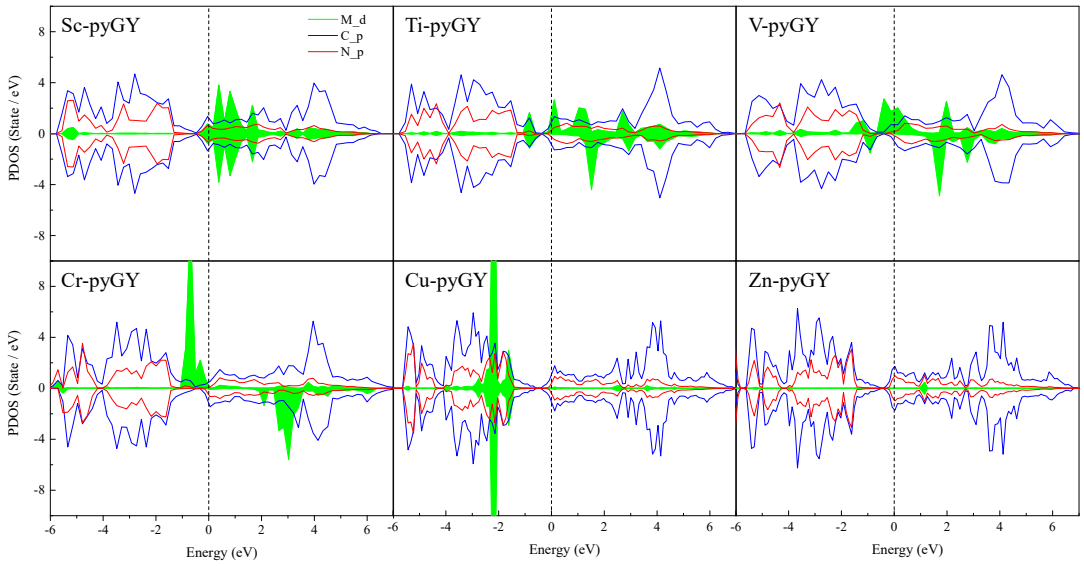

Fig. S4. PDOS of TM-pyGYs.

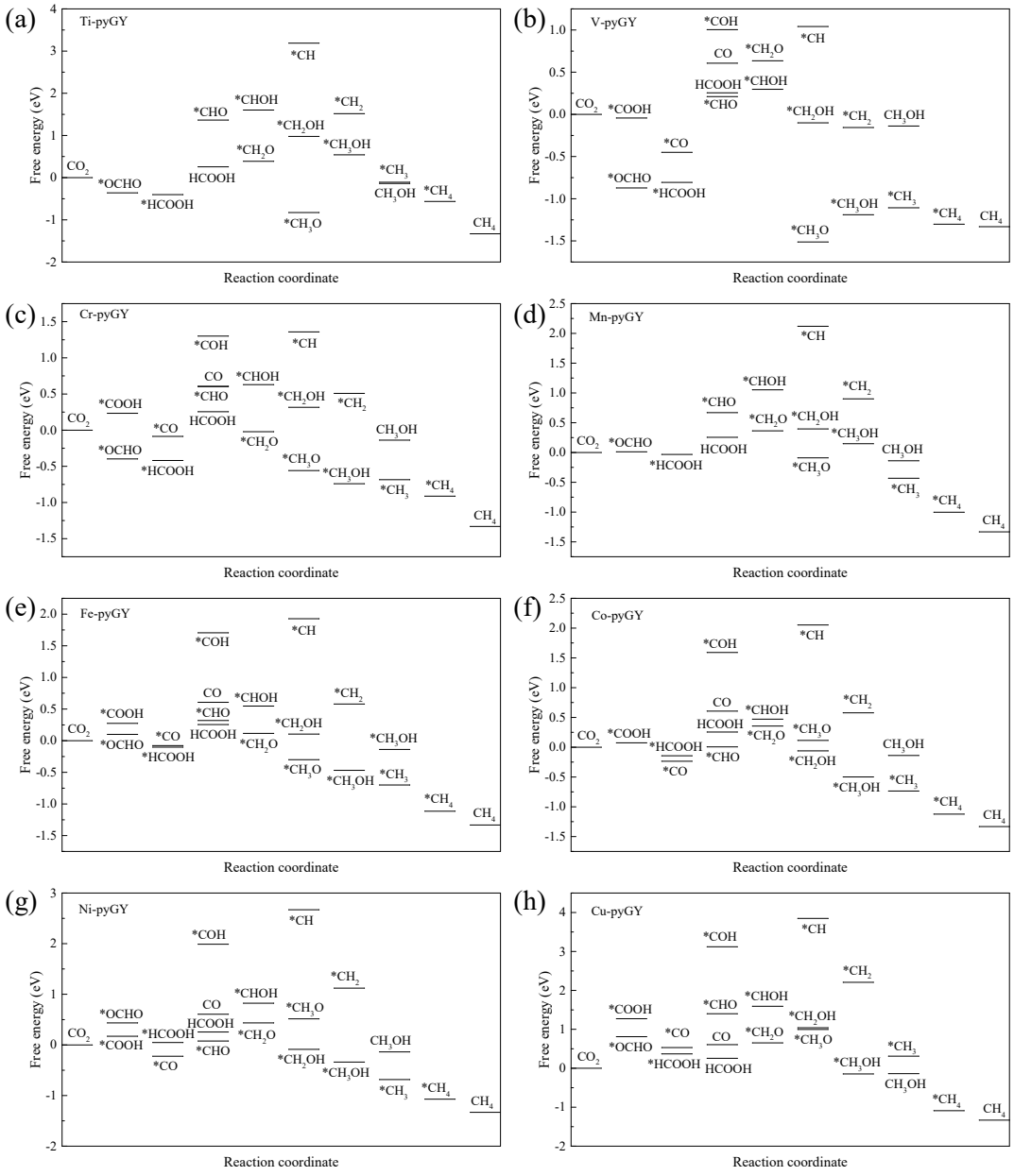

Fig. S5. The Gibbs free energy of all possible intermediates in CO_2RR on TM-pyGYs.

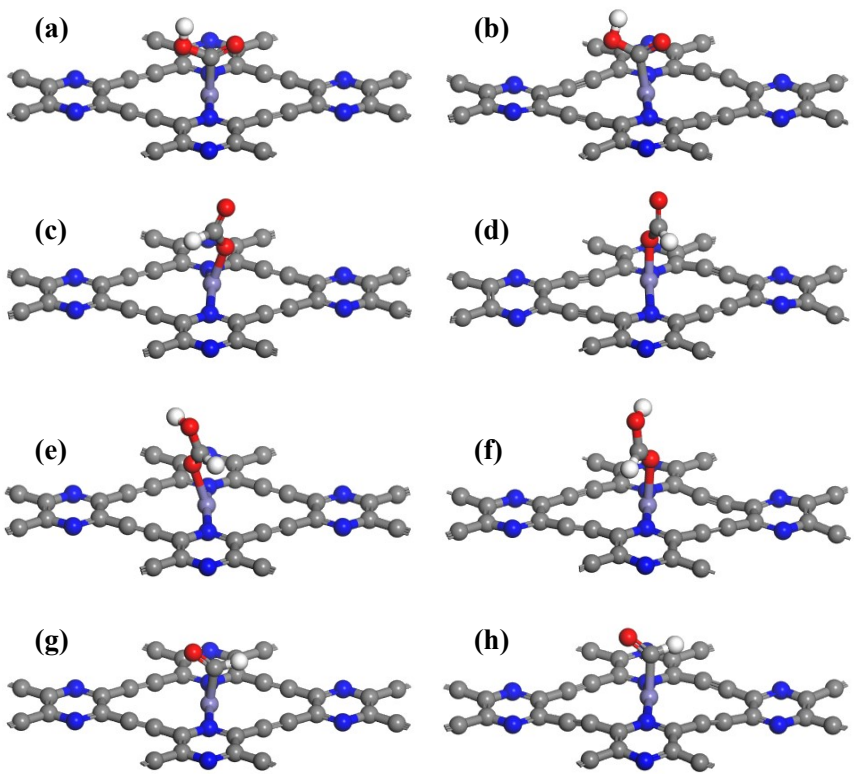

Fig. S6. The adsorption configurations of *COOH, *OCHO, *HCOOH, and *CHO on Fe-pyGY before (a, c, e, and g) and after (b, d, f, and g) molecular dynamics simulations.

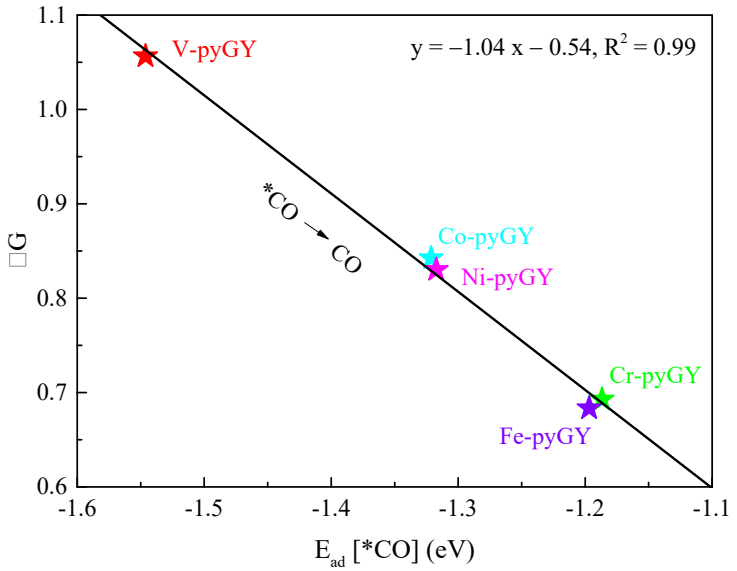

Fig. S7. ΔG of PLS as a function of *CO adsorption energy.

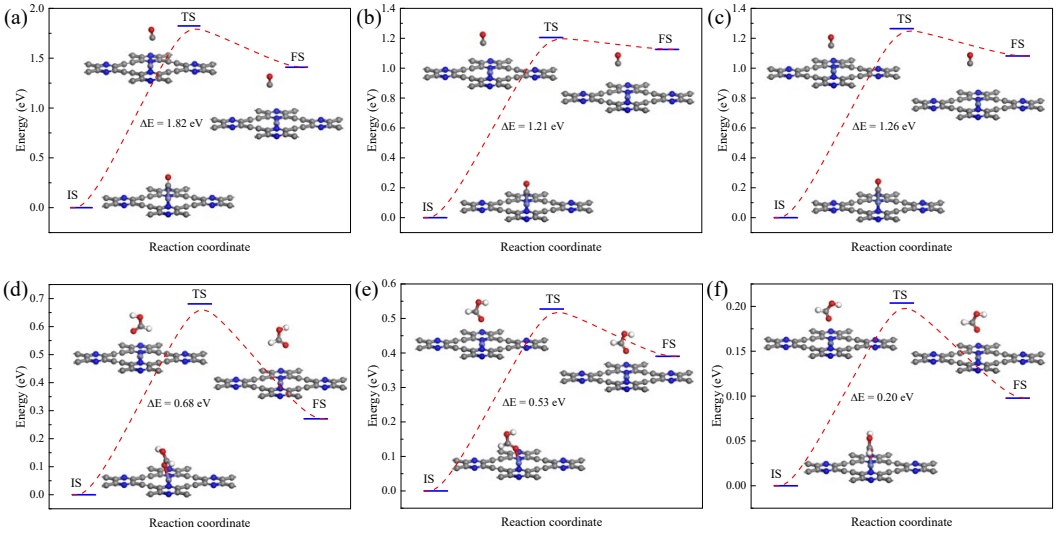

Fig. S8. Reaction kinetic of CO desorption on (a) Fe-pyGY, (b) Co-pyGY, and (c) Ni-pyGY and HCOOH desorption on (d) Fe-pyGY, (e) Co-pyGY, and (f) Ni-pyGY. The initial states (IS), transition states (TS), and final states (FS) are shown in the inset.

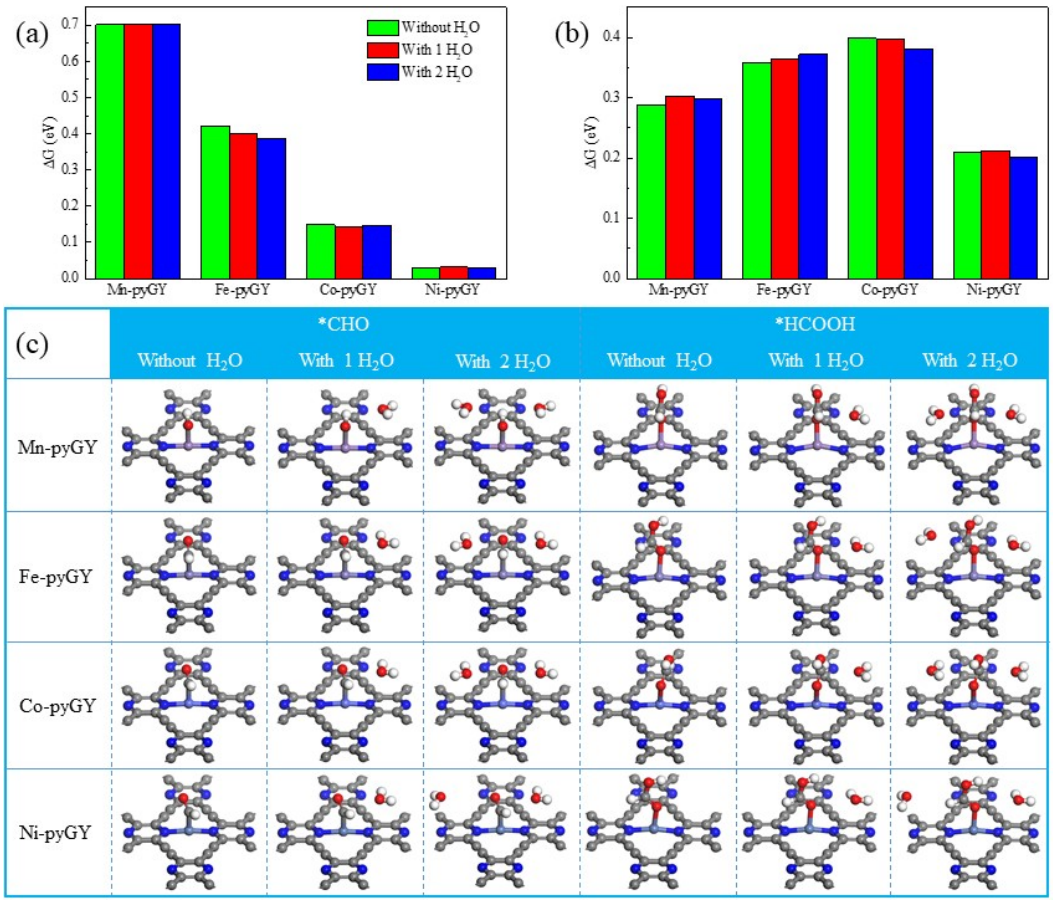

Fig. S9. Reaction free energies of (a) *HCOOH → *CHO and (b) HCOOH desorption on Mn/Fe/Co/Ni-pyGYs with/without explicit H_2O molecules. (c) Corresponding *CHO and *HCOOH adsorption configurations on Mn/Fe/Co/Ni-pyGYs.

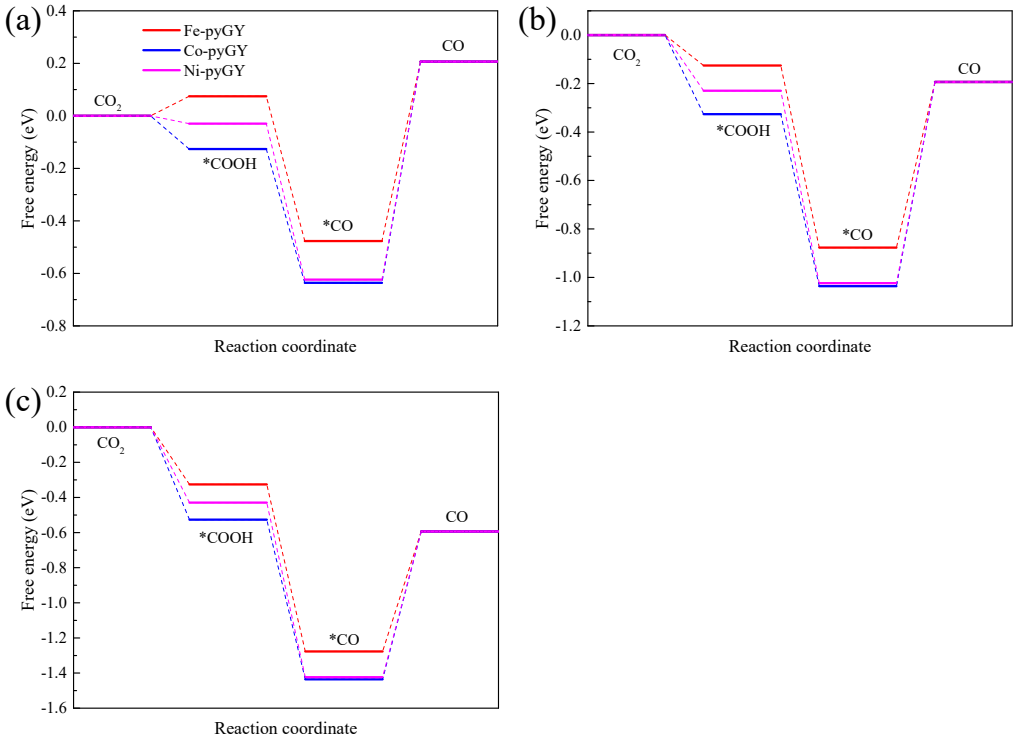

Fig. S10. Free energy diagrams of CO_2RR pathway to CO on TM-pyGYs at (a) –0.2 V, (b) –0.4 V, and (c) –0.6 V.

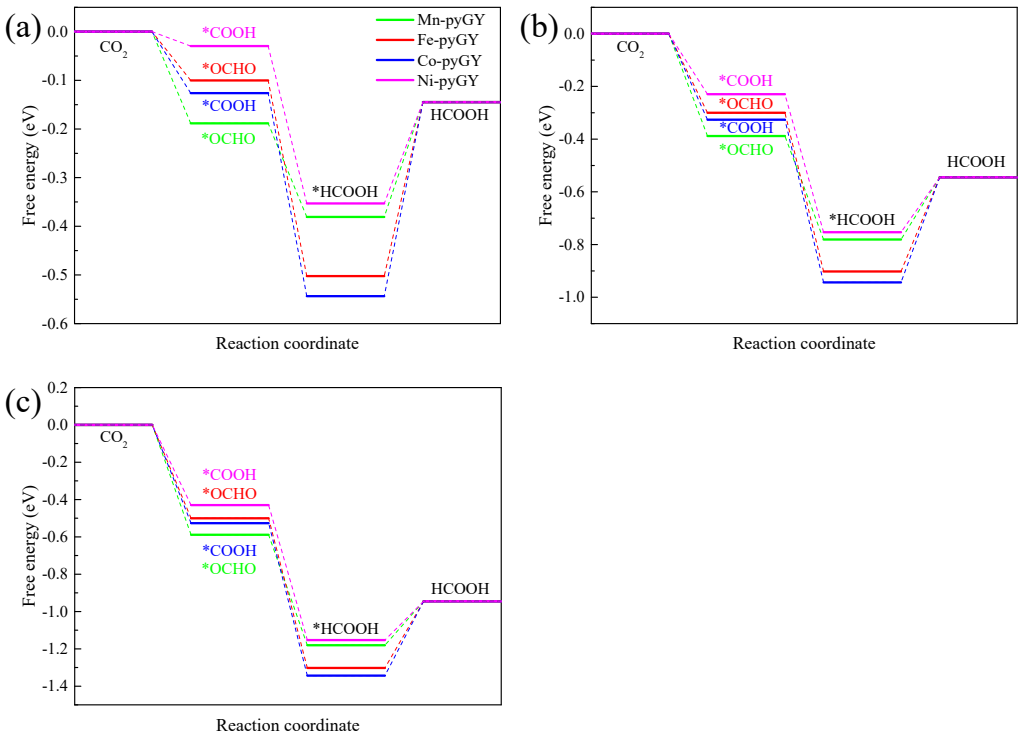

Fig. S11. Free energy diagrams of CO_2RR pathway to HCOOH on TM-pyGYs at (a) –0.2 V, (b) –0.4 V, and (c) –0.6 V.

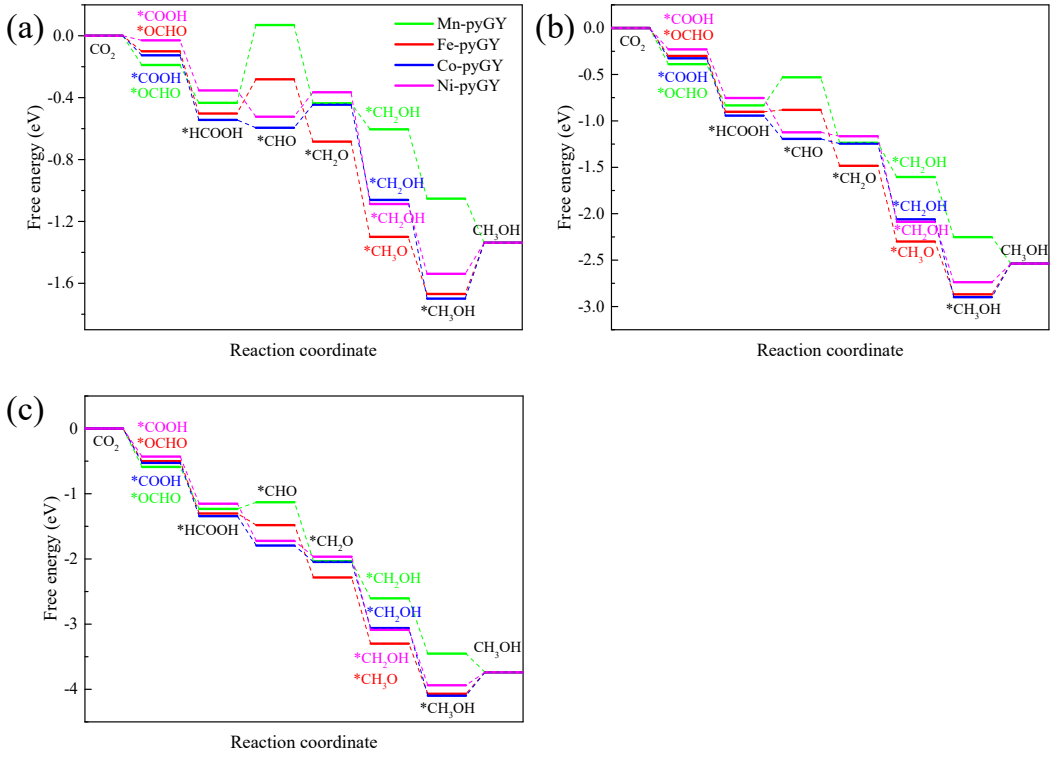

Fig. S12. Free energy diagrams of CO_2RR pathway to CH_3OH on TM-pyGYs at (a) –0.2 V, (b) –0.4 V, and (c) –0.6 V.

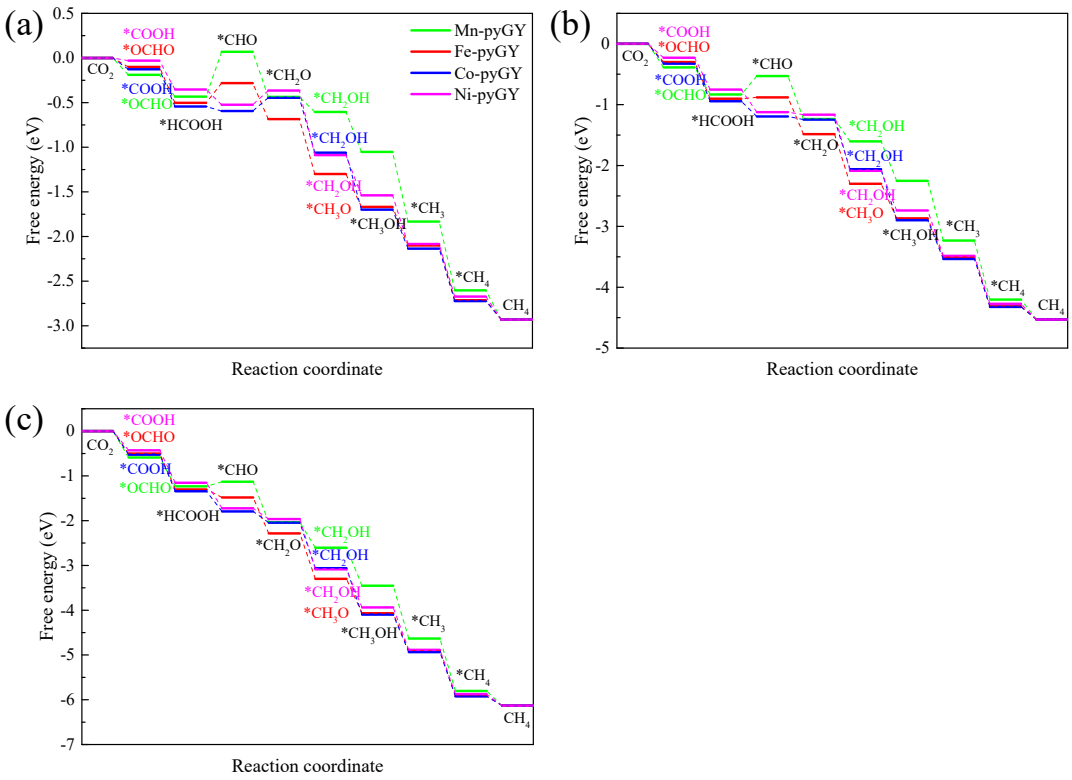

Fig. S13. Free energy diagrams of CO_2RR pathway to CH_4 on TM-pyGYs at (a) –0.2 V, (b) –0.4 V, and (c) –0.6 V.

References

1. S. Qi, X. Ma, B. Yang, L. Sun, W. Li, and M. Zhao, *Carbon*, 2019, **149**, 234−241.