Supporting Information (SI)

Electrochemical CO_2 reduction on TM-C_3N_5 for C1 products: A DFT study

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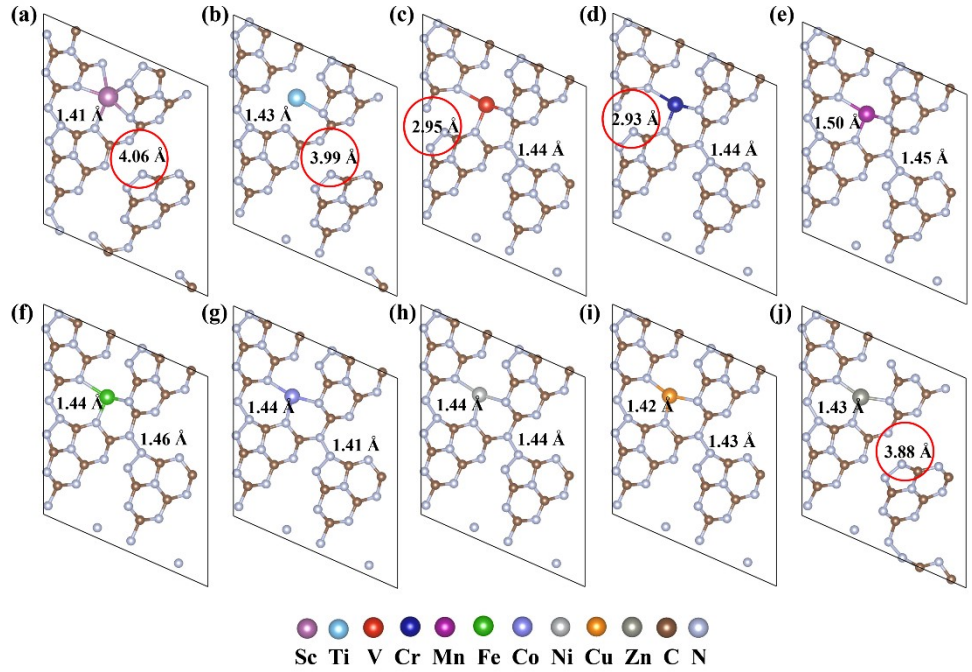


Figure S1 Optimized structure of TM-C_3N_5 (TM = Sc ~ Zn).

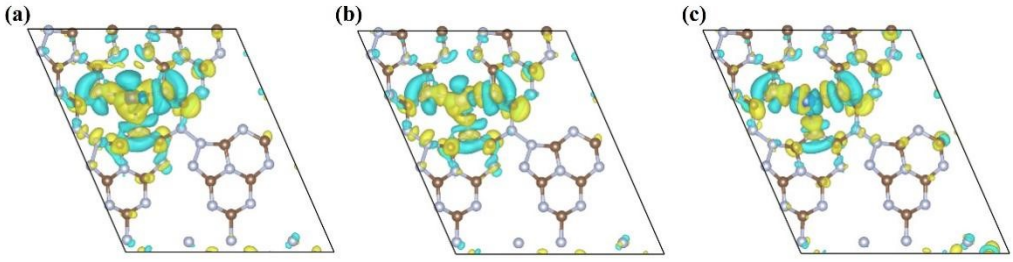


Figure S2. Isosurface of charge density difference (Δρ) for TM-C_3N_5 (TM = Co, Ni, Cu). Yellow: charge accumulation; cyan: charge depletion. Isosurface level = 0.002 e Bohr $^{-3}$.

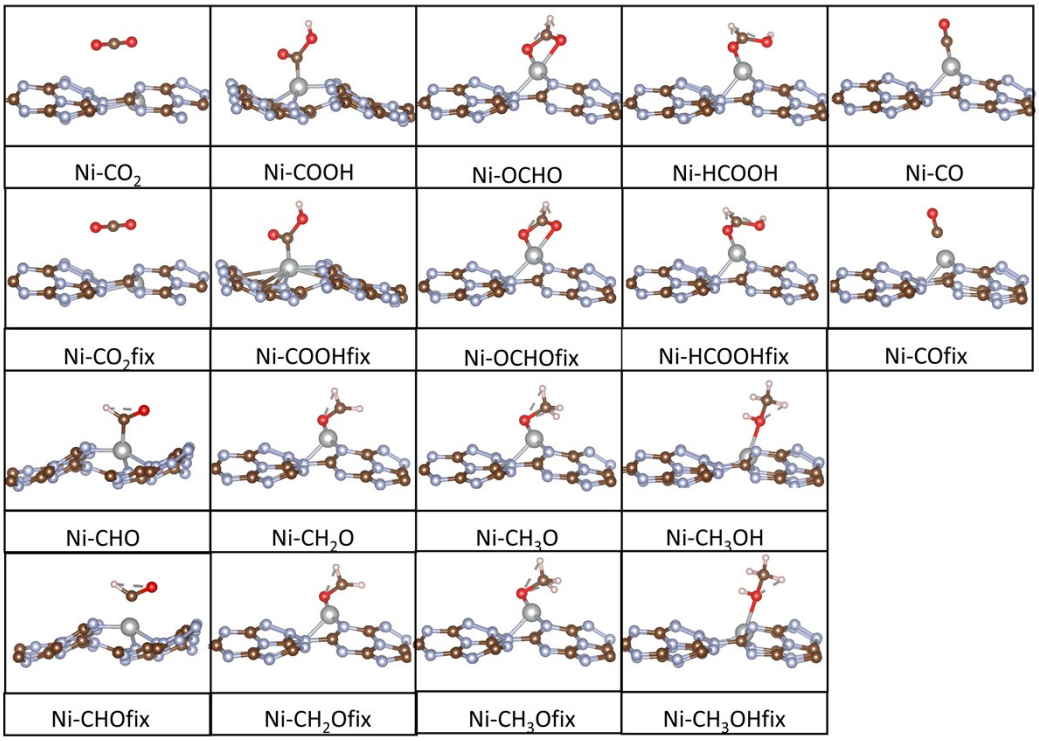


Figure S3. Optimized configuration and energy supplementation of fixing C_3N_5.

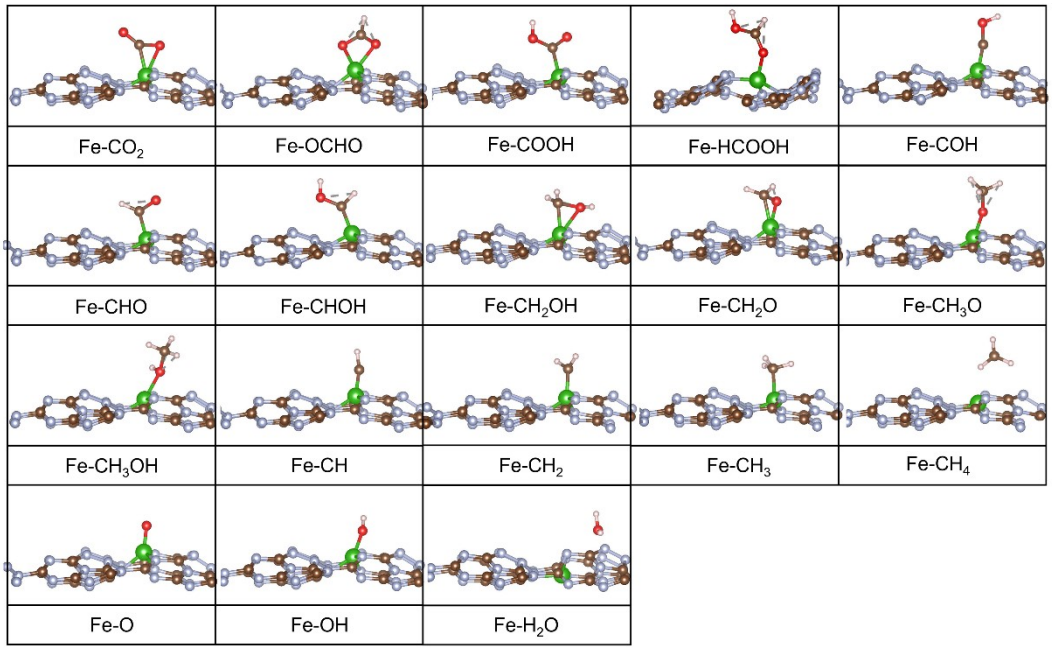


Figure S4. Optimized configurations of all intermediates on Fe-C_3N_5.

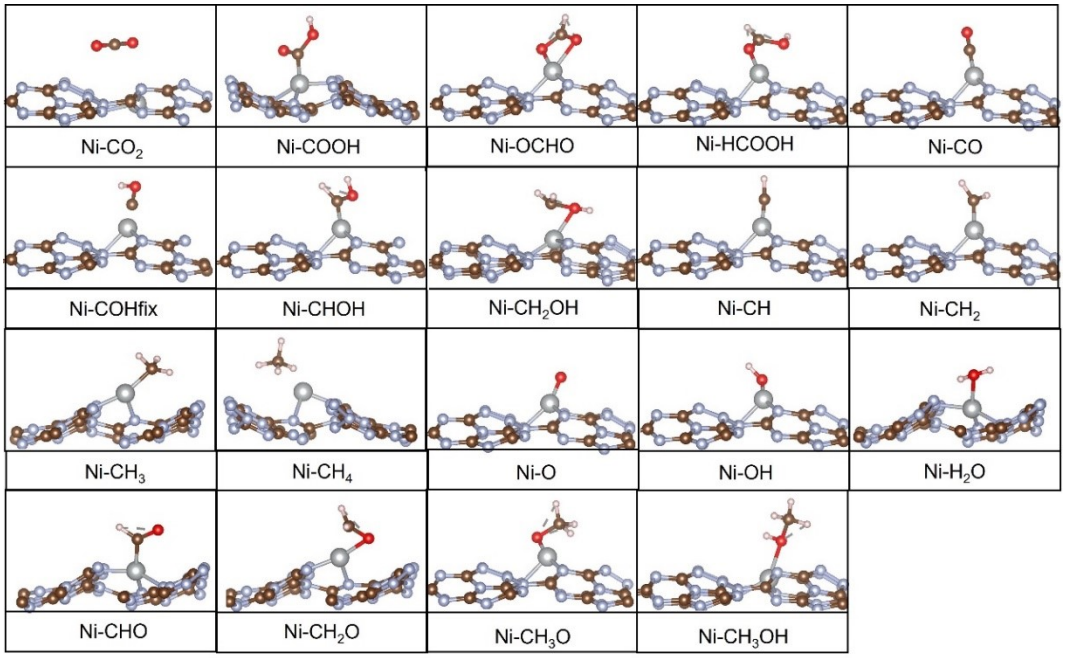


Figure S5. Optimized configurations of all intermediates on Ni-C_3N_5.

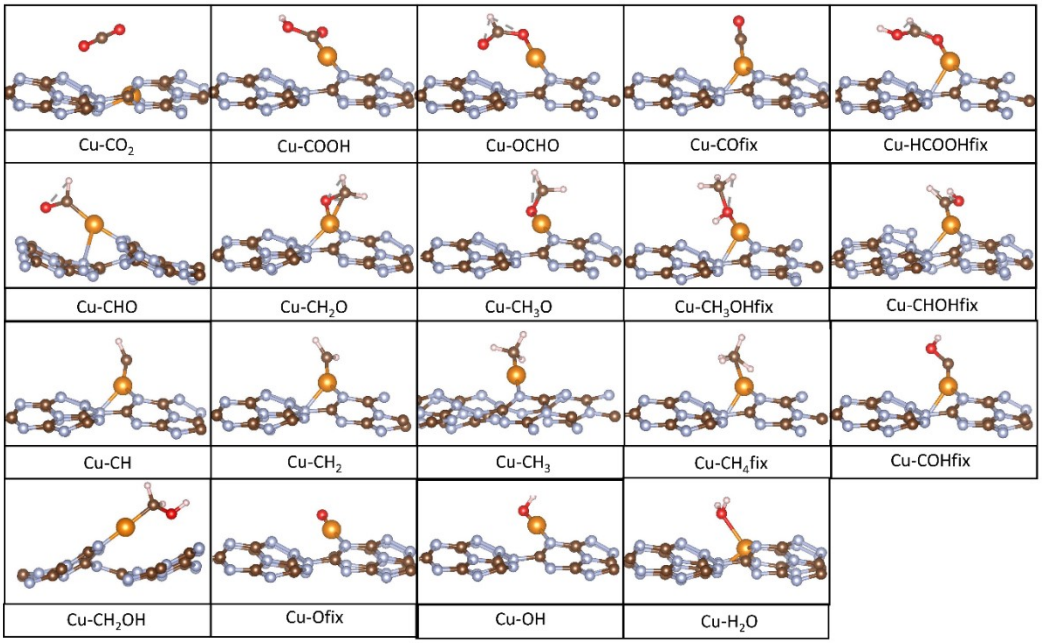
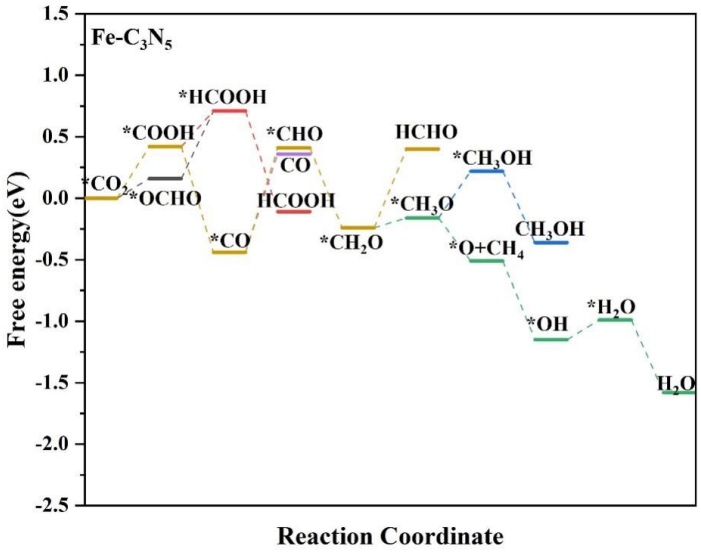
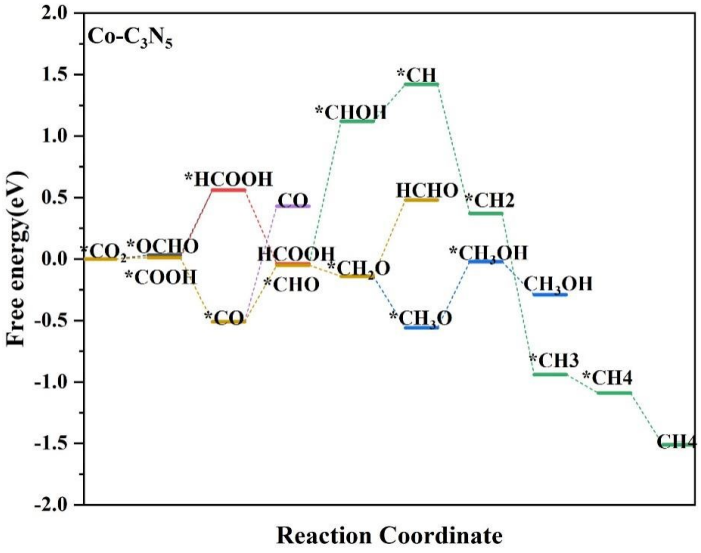


Figure S6. Optimized configurations of main intermediates on Cu-C_3N_5.

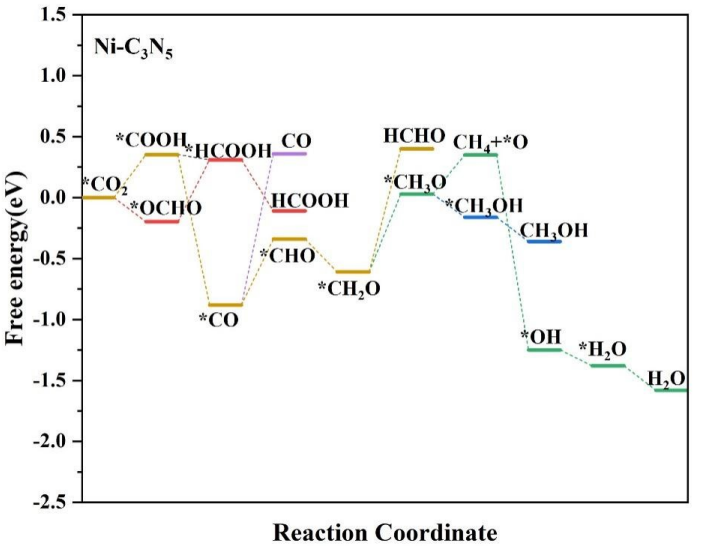
(a)


Fe-C3N5
Free energy(eV)
Reaction Coordinate
*CO2
*OCHO
*COOH
*HCOOH
*CO
*CHO
CO
HCOOH
*CH2O
HCHO
*CH3O
*CH3OH
CH3OH
*O+CH4
*OH
*H2O
H2O

(b)


Co-C3N5
Free energy(eV)
Reaction Coordinate
*CO2
*OCHO
*COOH
*HCOOH
*CO
*CHO
CO
HCOOH
*CH2O
*CHOH
*CH
HCHO
*CH2
*CH3O
*CH3OH
CH3OH
*CH3
*CH4
CH4

(c)


Ni-C3N5
Free energy(eV)
Reaction Coordinate
*CO2
*OCHO
*COOH
*HCOOH
*CO
*CHO
CO
HCOOH
*CH2O
HCHO
*CH3O
CH4+*O
*CH3OH
CH3OH
*OH
*H2O
H2O

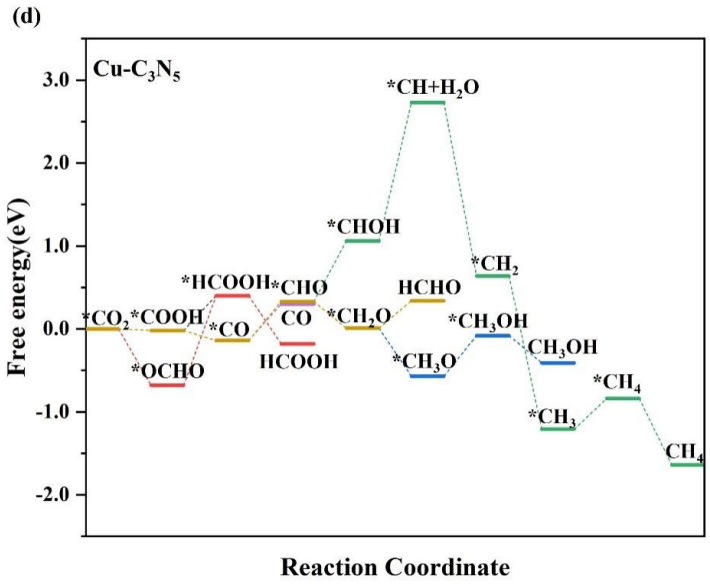
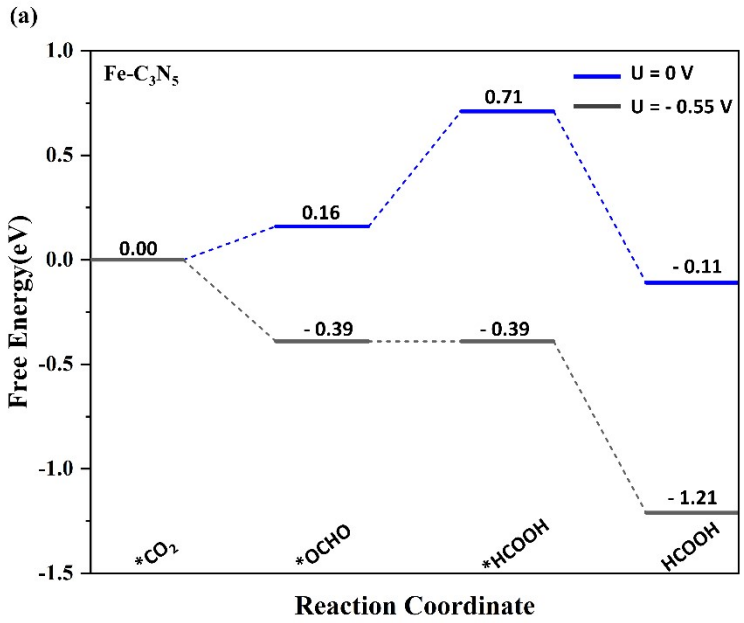
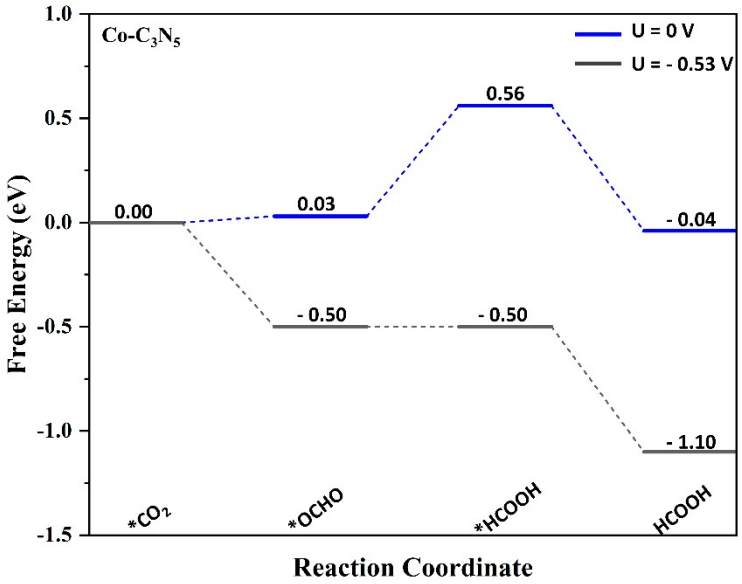


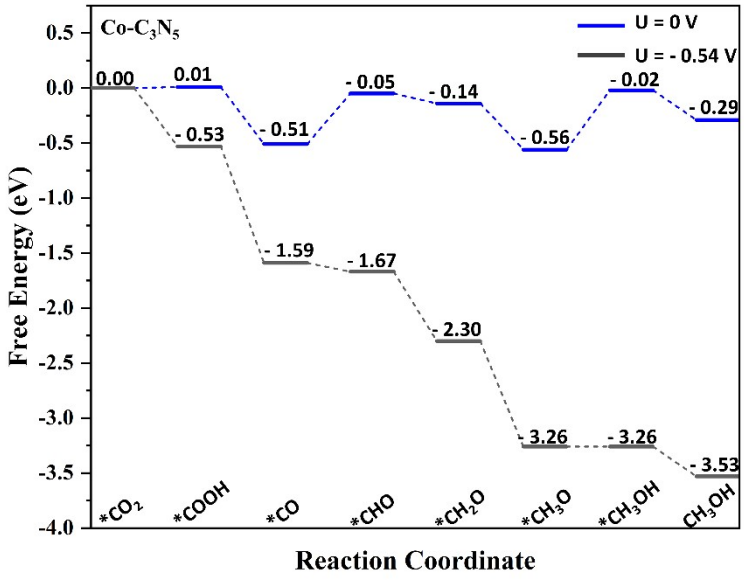
Figure S7. (a), (b), (c), (d) all reduction pathways on Fe- C_3N_5, Co- C_3N_5, Ni-C_3N_5 and Cu-C_3N_5.



(b)


Co-C3N5
U = 0 V
U = - 0.53 V
Free Energy (eV)
1.0
0.5
0.0
-0.5
-1.0
-1.5
0.00
0.03
0.56
- 0.04
- 0.50
- 0.50
- 1.10
*CO2
*OCHO
*HCOOH
HCOOH
Reaction Coordinate

(c)


Co-C3N5
U = 0 V
U = - 0.54 V
Free Energy (eV)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
0.00
0.01
- 0.05
- 0.14
- 0.02
- 0.29
- 0.53
- 0.51
- 0.56
- 1.59
- 1.67
- 2.30
- 3.26
- 3.26
- 3.53
*CO2
*COOH
*CO
*CHO
*CH2O
*CH3O
*CH3OH
CH3OH
Reaction Coordinate

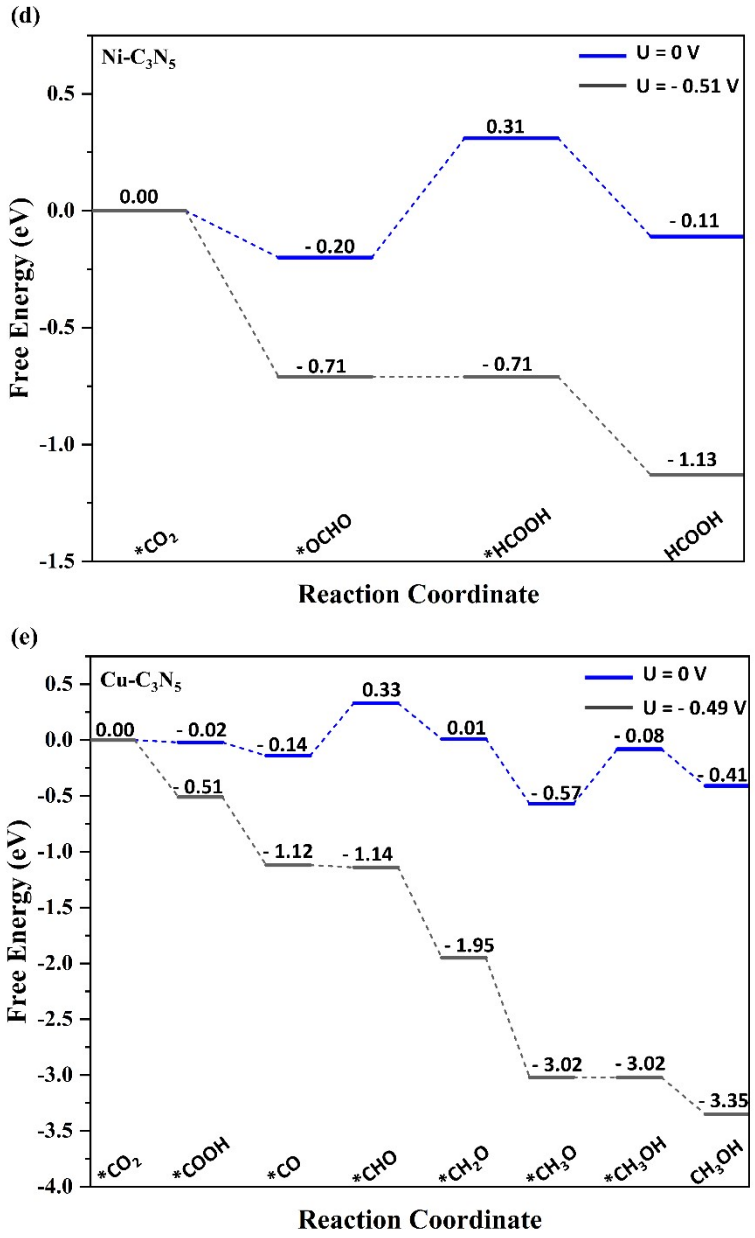


Figure S8. (a), (b), (d) The HCOOH generated on Fe-C_3N_5, Co-C_3N_5 and Ni-C_3N_5 vs the HCOOH generated on Fe-C_3N_5, Co-C_3N_5 and Ni-C_3N_5 with applied voltage, (c), (e) The CH_3OH generated on Co-C_3N_5 and Cu-C_3N_5 vs the CH_3OH generated on Co-C_3N_5 and Cu-C_3N_5 with applied voltage.

	Eads(eV)	C-O(Å)	C-O1'(Å)	C-O2'(Å)	Q1(before)	Q2(after)	ΔQ(e)
Fe	-0.84	1.18	1.27	1.21	16	16.53	0.53
Co	-0.55	1.18	1.26	1.21	16	16.45	0.45
Ni	-0.23	1.18	1.18	1.18	16	16.03	0.03
Cu	-0.20	1.18	1.18	1.18	16	16.02	0.02

Table S1. Adsorption energy (E_{ads}), C-O bond distance difference and Bader charge for CO_2 adsorbed on TM-C_3N_5.

Intermediates	E_{relax}(eV)	E_{fix}(eV)
Ni-CO_2	-457.17	-457.17
Ni-COOH	-460.57	460.57
Ni-OCHO	-461.13	-461.14
Ni-HCOOH	-464.27	-464.27
Ni-CO	-450.58	-450.40
Ni-CHO	-453.75	-453.17
Ni-CH_2O	-457.70	-457.70
Ni-CH_3O	-460.71	-460.71
Ni-CH_3OH	-464.59	-464.59

Table S2. Energy comparison of all optimal method versus partial optimal method on Ni-C_3N_5.

Adsorbate	E(eV)	ZPE-TS(eV)	G(eV)
Fe-CO_2	-459.69	0.23	-459.46
Fe-OCHO	-463.24	0.54	-462.69
Fe-COOH	-462.92	0.49	-462.44
Fe-CO	-452.61	0.13	-452.48
Fe-COH	-454.47	0.50	-453.98
Fe-CHOfix	-455.40	0.37	-455.02
Fe-CH_2O	-459.80	0.73	-459.07
Fe-CH_3O	-463.36	0.97	-462.39
Fe-CH_3OHfix	-466.70	1.28	-465.41
Fe-O	-442.80	0.02	-442.78
Fe-OH	-447.13	0.31	-446.82
Fe-H_2O	-450.61	0.55	-450.06
Fe-CHOH	-458.38	0.68	-457.70
Fe-CH_2OH	-462.92	1.03	-461.88
Fe-CH	-446.88	0.29	-446.59
Fe-CH_2	-451.56	0.58	-450.98
Fe-CH_3	-456.10	0.88	-455.23
Fe-CH_4	-459.89	1.04	-458.85
Fe-HCOOH	-466.32	0.78	-465.54

Table S3. Total energy of the intermediates adsorbed on the surface of Fe-C_3N_5.

Adsorbate	E(eV)	ZPE-TS(eV)	G(eV)
Co-CO_2	-458.41	0.22	-458.20
Co-COOH	-462.09	0.50	-461.59
Co-OCHO	-462.10	0.53	-461.57
Co-COH	-453.65	0.38	-453.27
Co-CHOH	-457.13	0.67	-456.46
Co-CH_2OH	-461.87	0.99	-460.87
Co-CH_3OH	-465.68	1.29	-464.40
Co-CHO	-454.62	0.39	-454.23
Co-CH_2O	-458.43	0.70	-457.73
Co-CH_3O	-462.53	0.98	-461.54
Co-CH	-445.81	0.47	-445.34
Co-CH_2	-450.39	0.59	-449.80
Co-CH_3	-455.40	0.89	-454.51
Co-CH_4	-459.09	1.04	-458.06
Co-HCOOH	-465.22	0.79	-464.44
Co-O	-439.11	0.04	-439.08
Co-OH	-446.36	0.33	-446.03
Co-H_2O	-449.86	0.64	-449.22

Table S4. Total energy of the intermediate adsorbed on the surface of Co-C_3N_5.

Adsorbate	E(eV)	ZPE-TS(eV)	G(eV)
Ni-CO_2	-457.17	0.17	-457.01
Ni-COOH	-460.57	0.51	-460.05
Ni-OCHO	-461.13	0.53	-460.60
Ni-CO	-450.58	0.12	-450.46
Ni-COHfix	-452.13	0.38	-451.75
Ni-CHOH	-456.40	0.68	-455.72
Ni-CH_2OH	-460.24	1.04	-459.20
Ni-CH_3OH	-464.59	1.25	-463.34
Ni-CHO	-453.75	0.43	-453.32
Ni-CH_2O	-457.70	0.71	-456.99
Ni-CH_3O	-460.71	0.96	-459.75
Ni-CH	-444.08	0.28	-443.80
Ni-CH_2	-449.19	0.57	-448.62
Ni-CH_3	-453.64	0.84	-452.80
Ni-CH_4	-457.97	1.13	-456.84
Ni-HCOOH	-464.27	0.78	-463.49
Ni-O	-439.48	0.01	-439.47
Ni-OH	-444.76	0.30	-444.47
Ni-H_2O	-448.62	0.62	-448.00

Table S5. Total energy of the intermediate adsorbed on the surface of Ni-C_3N_5.

Adsorbate	E(eV)	ZPE-TS(eV)	G(eV)
Cu-CO_2	-455.51	0.17	-455.35
Cu-COOH	-459.24	0.48	-458.77
Cu-OCHO	-459.91	0.49	-459.42
Cu-COfix	-448.18	0.11	-448.07
Cu-HCOOHfix	-462.53	0.78	-461.75
Cu-CHO	-451.39	0.39	-451.00
Cu-CH_2O	-455.42	0.69	-454.72
Cu-CH_3O	-459.68	0.97	-458.71
Cu-CH_3OHfix	-462.91	1.29	-461.62
Cu-COH	-449.54	0.37	-449.17
Cu-CHOHfix	-454.34	0.67	-453.67
Cu-CH_2OH	-459.02	0.97	-458.05
Cu-CH	-441.44	0.26	-441.19
Cu-CH_2	-447.24	0.56	-446.68
Cu-CH_3	-452.77	0.84	-451.93
Cu-CH_4fix	-456.09	1.13	-454.96
Cu-Ofix	-437.05	0.01	-437.05
Cu-OH	-443.65	0.28	-433.36
Cu-H_2O	-466.98	0.51	-466.47

Table S6. Total energy of the intermediate adsorbed on the surface of Cu-C_3N_5.

Molecules	E(eV)	ZPE-TS(eV)	G(eV)
H_2(g)	-6.76	-0.04	-6.80
H_2O(l)	-14.22	0.00	-14.22
CO(g)	-14.78	-0.46	-15.24
HCOOH(l)	-29.89	-0.05	-29.93
HCHO(g)	-22.13	0.13	-22.00
CH_3OH(g)	-30.22	0.66	-29.56
CH_4(g)	-24.04	0.67	-23.37

Table S7. Total energy of gaseous molecules and CO_2 reduction products. Saturation vapor pressure for correcting energy Vapor pressure values are quoted in Peterson et al[1].

References

1. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Nørskov, *Energy & Environmental Science*, 2010, **3**.