Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Boosting Photo-assisted efficient Electrochemical CO_2 Reduction Reaction on Transition Metal Single-Atom Catalysts Supported on C_6N_6 nanosheet: A Computational Study

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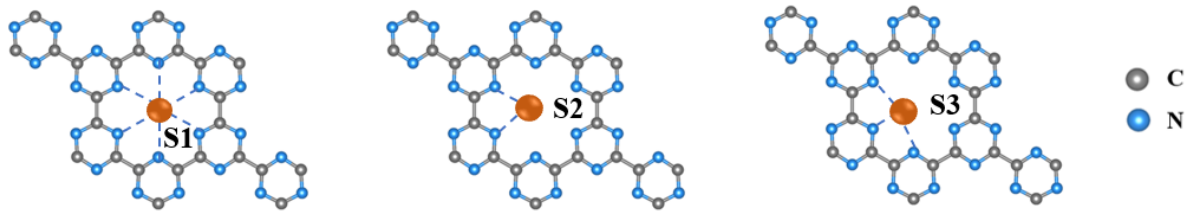


Figure S1. Optimized geometry of C_6N_6 nanosheet and various possible adsorption sites (S1, S2, S3) considered on the surface for doping single TM atom (TM = Fe, Co, Ni).

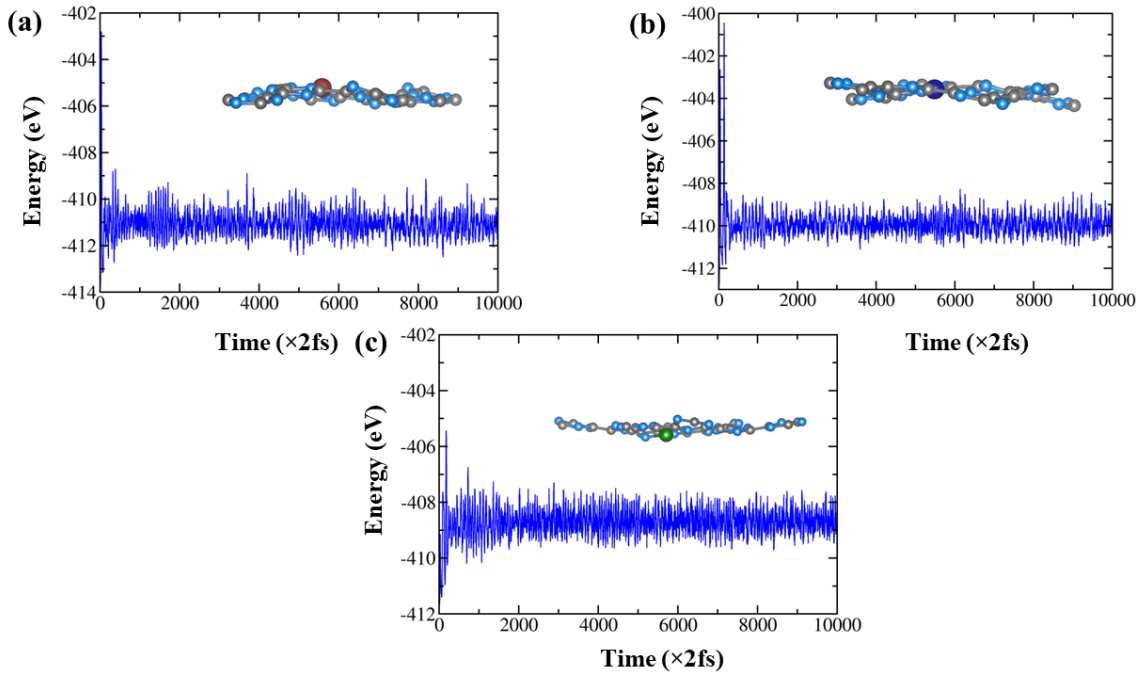


Figure S2. Variation of energy with time for AIMD simulation of (a) Fe@C_6N_6, (b) Co@C_6N_6 and, (c) Ni@C_6N_6 sheet at 500 K for a period of 20 ps with a time step of 2 fs.

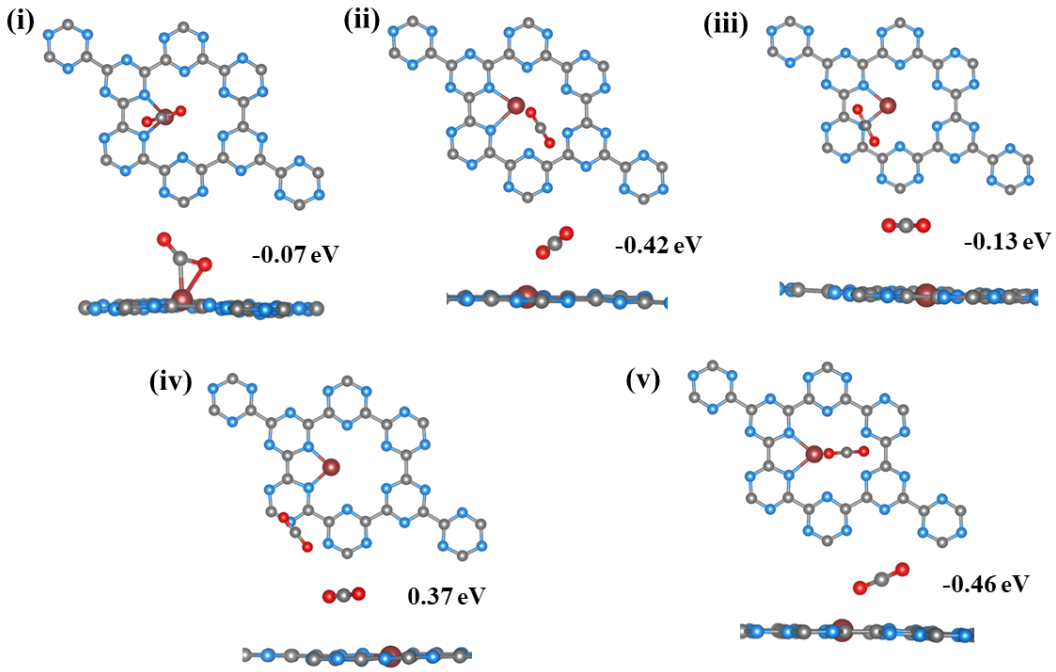


Figure S3. Optimized adsorption configurations for CO_2 adsorption and the corresponding adsorption energies (in eV) on $Fe@C_6N_6$.

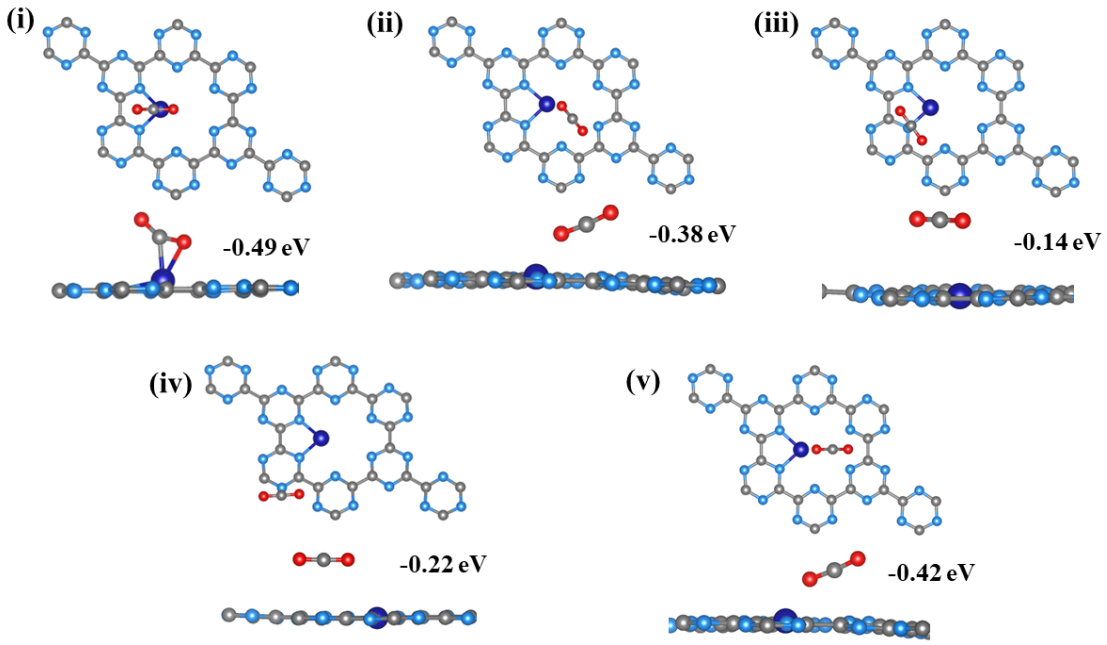


Figure S4. Optimized adsorption configurations for CO_2 adsorption and the corresponding adsorption energies (in eV) on $Co@C_6N_6$.

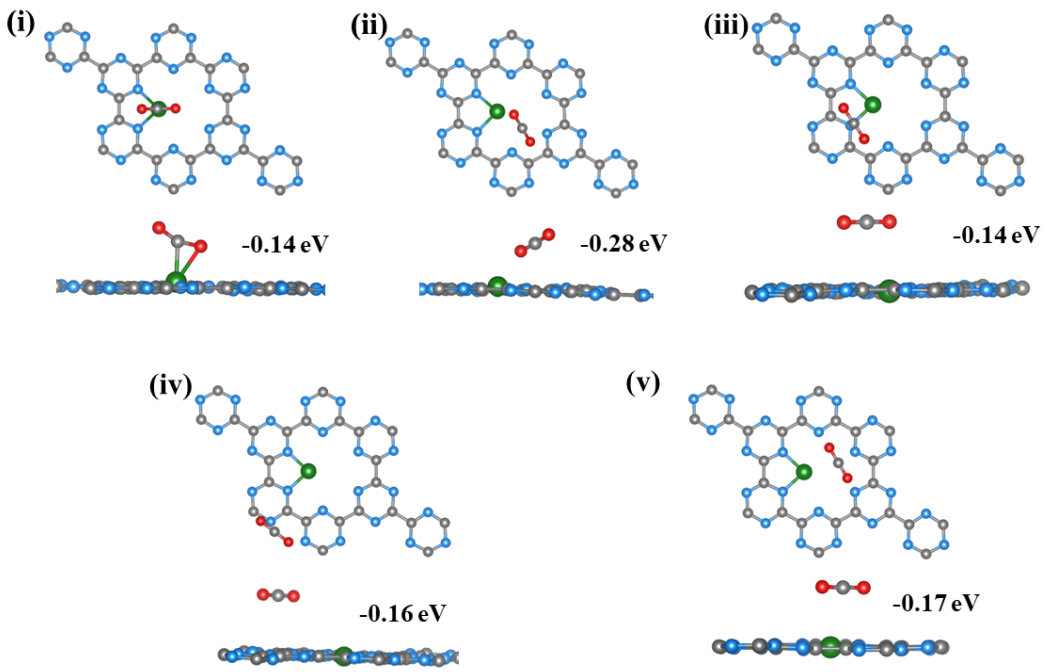
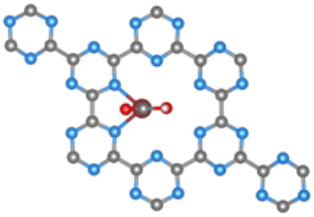
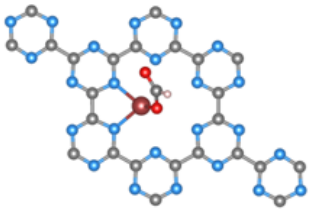


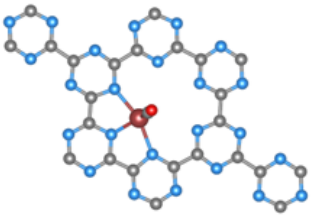
Figure S5. Optimized adsorption configurations for CO_2 adsorption and the corresponding adsorption energies (in eV) on $Ni@C_6N_6$.



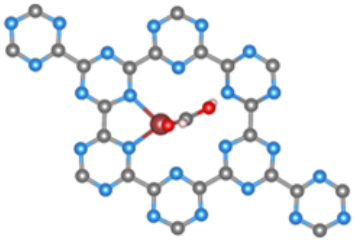
*COOH



*OCHO



*CO



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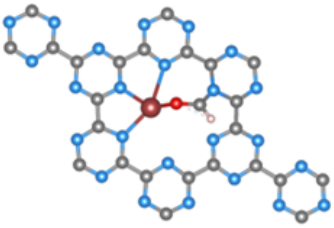

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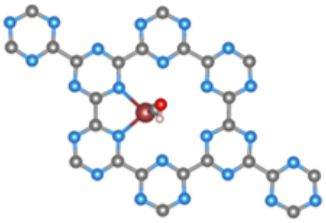

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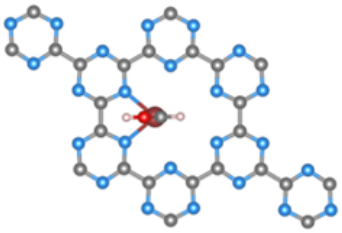
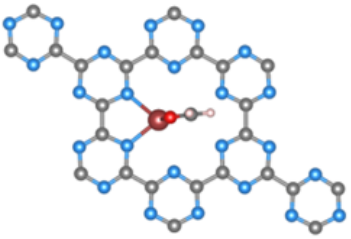


*CHOH



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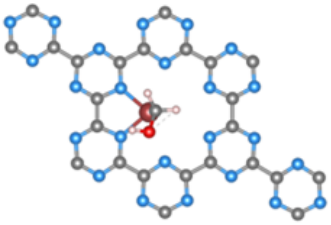

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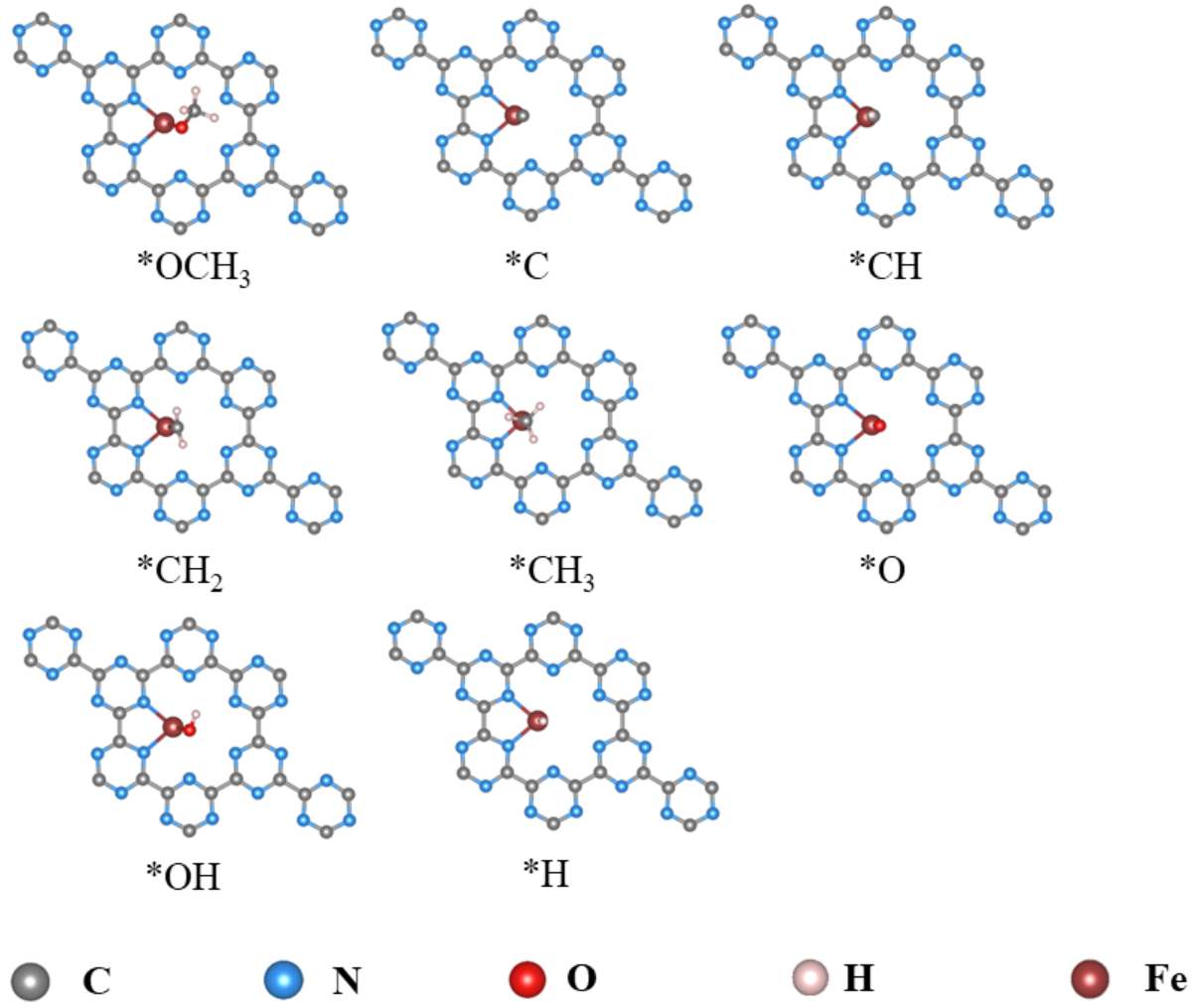
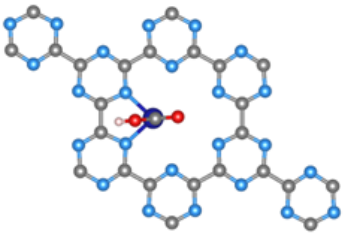


Figure S6. Optimized geometries for the intermediates along CO_2RR pathway on Fe@C_6N_6



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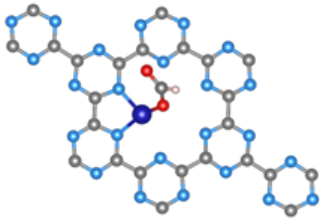
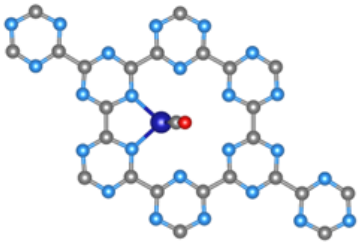
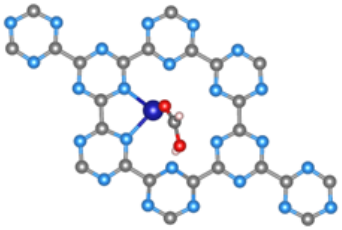


*OCHO



*CO



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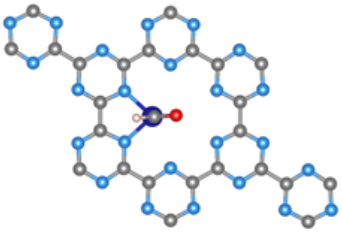

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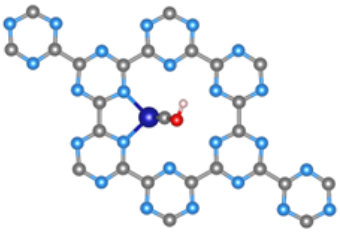

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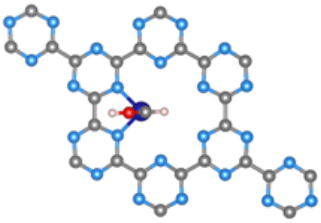

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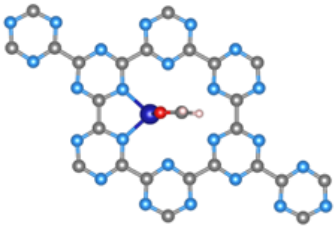

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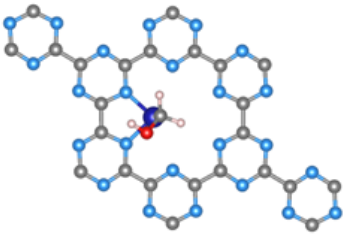

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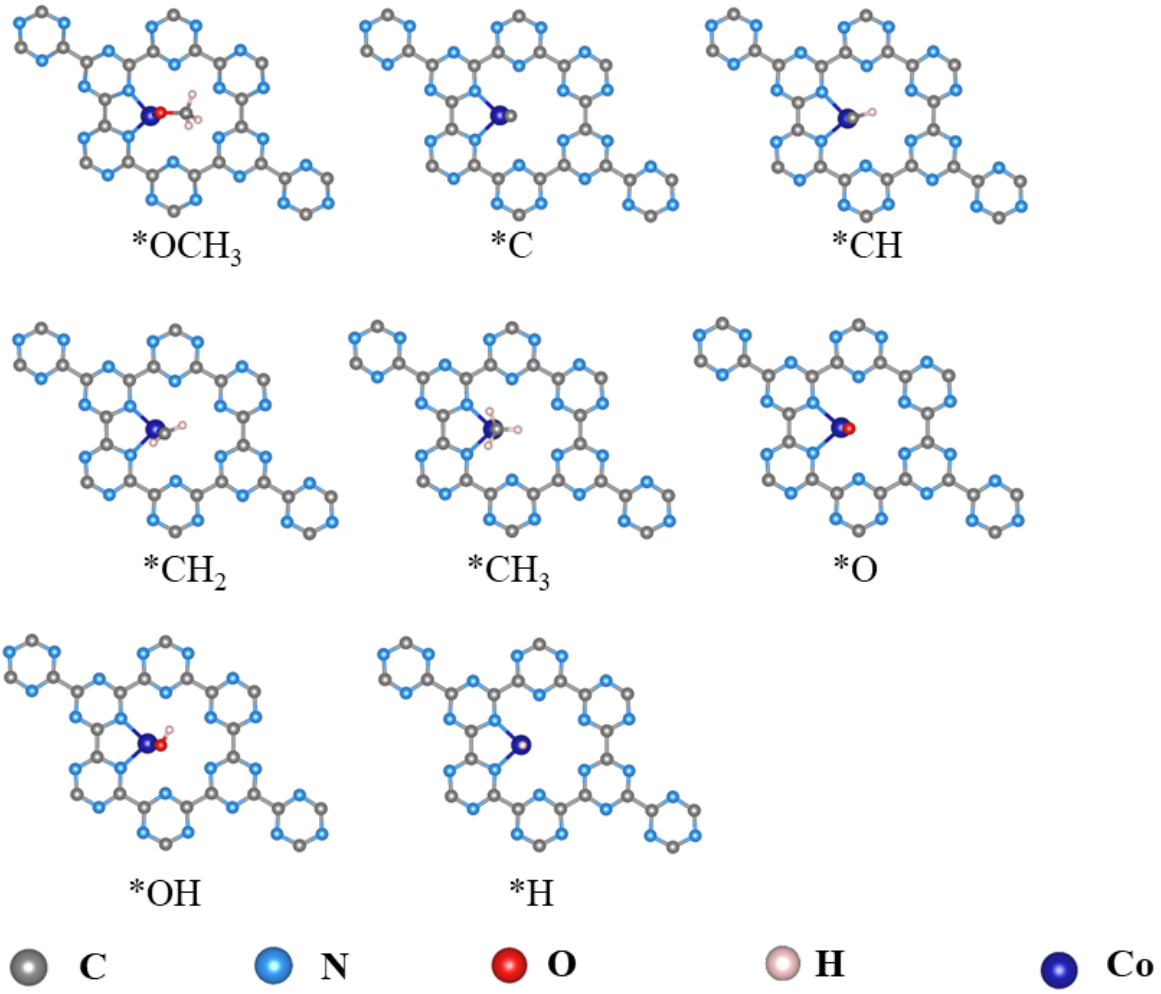
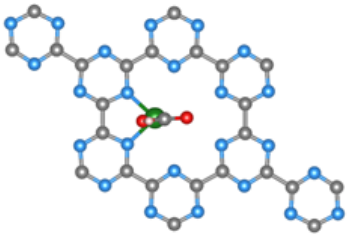


Figure S7. Optimized geometries for the intermediates along CO_2RR pathway on Co@C_6N_6



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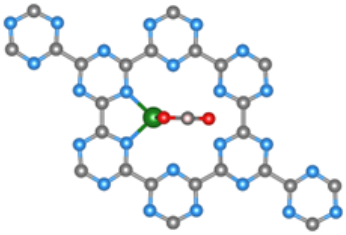

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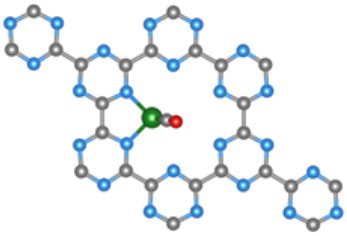

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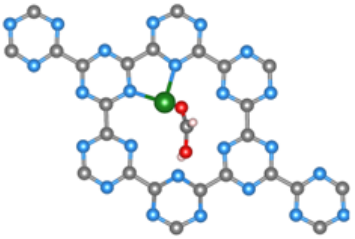
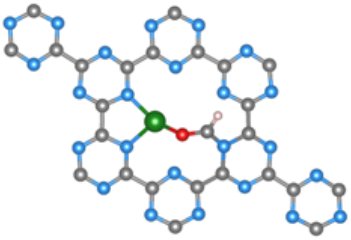


*HCOOH



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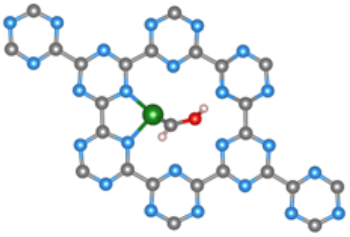
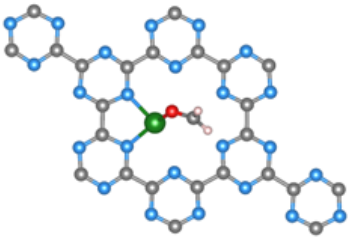
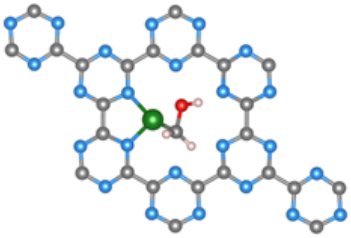


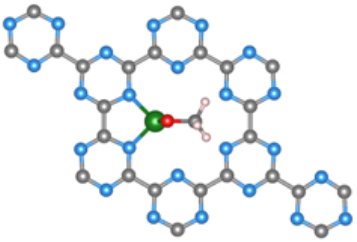
*CHOH



*OCH_2



*CH_2OH



*OCH_3

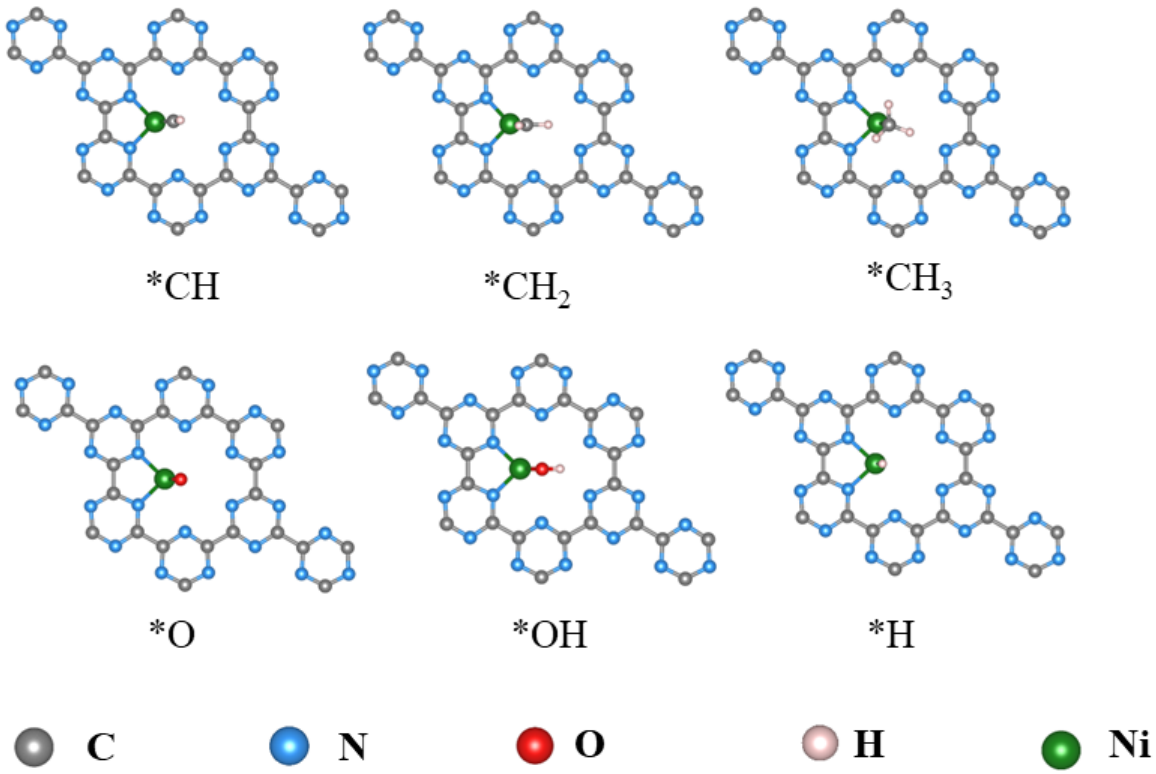
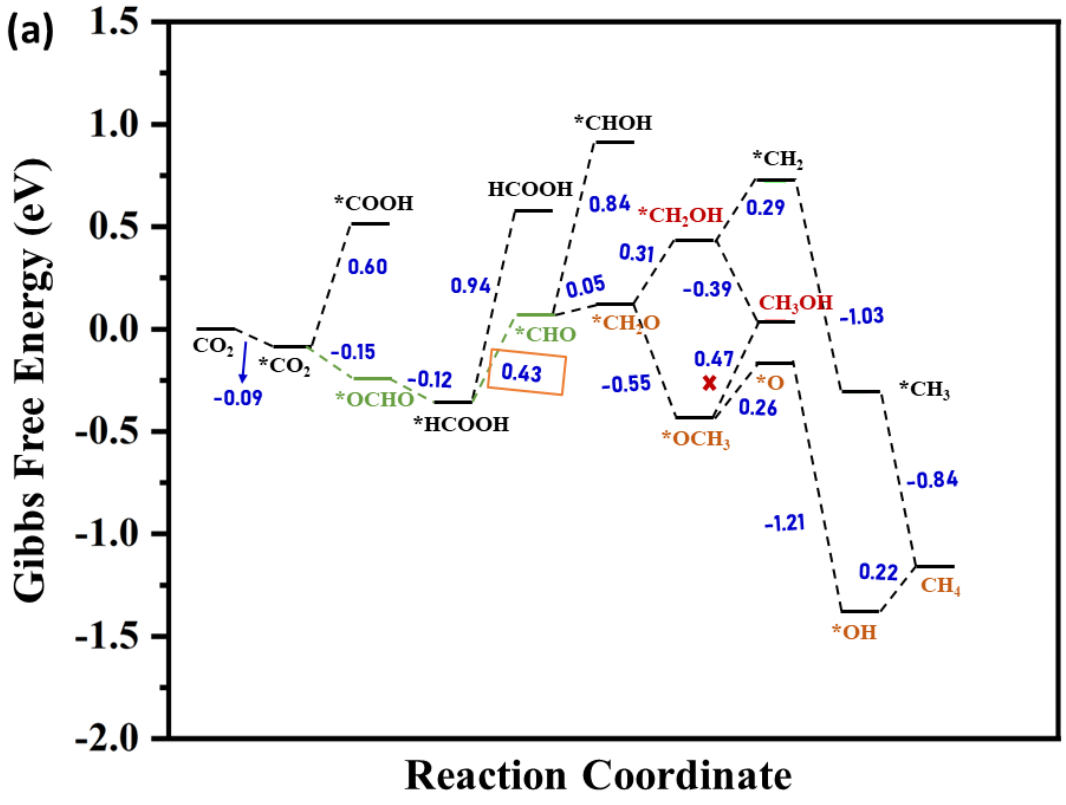


Figure S8. Optimized geometries for the intermediates along CO_2RR pathway on Ni@C_6N_6



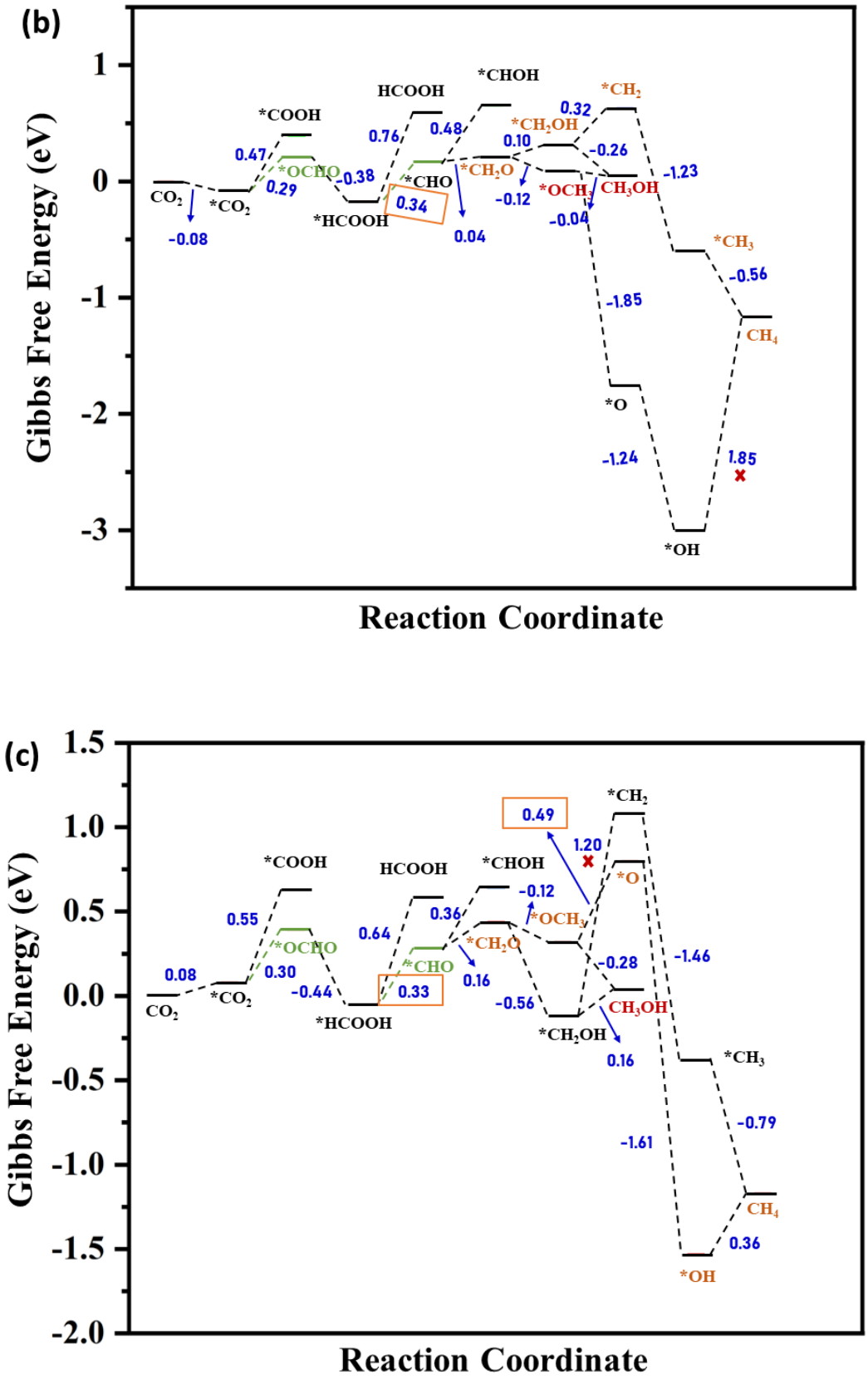


Figure S9. The complete Gibbs Free energy profile for CO_2RR on (a) Fe@C_6N_6, (b) Co@C_6N_6 and (c) Ni@C_6N_6 nanosheet.

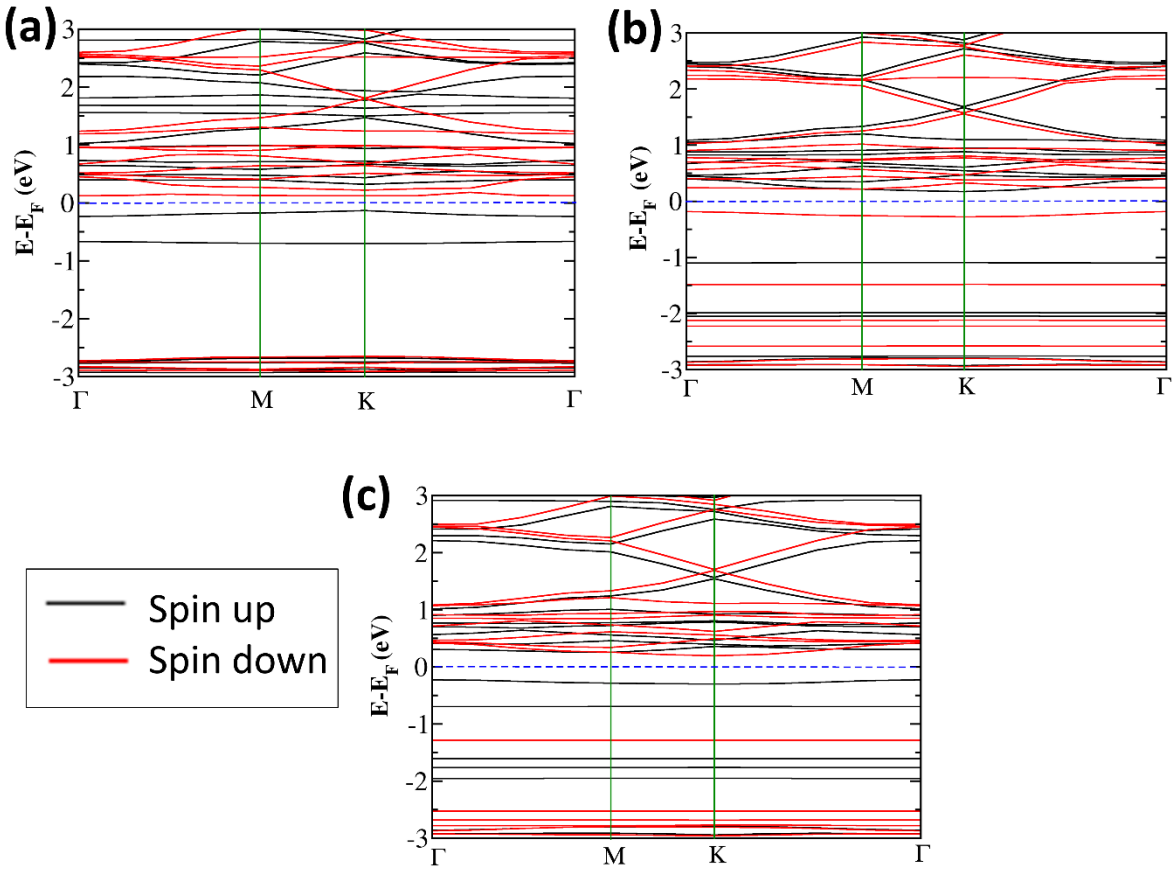


Figure S10. The spin-polarised band structures of the (a) Fe@C_6N_6, (b) Co@C_6N_6 and, (c) Ni@C_6N_6 sheet from the HSE06 functional.

	ZPE	TS
CO_2	0.31	0.66
CO	0.14	0.61
H_2	0.28	0.40
H_2O	0.57	0.58
HCOOH	0.89	0.77
CH_3OH	1.36	0.74
CH_4	1.19	0.58

Table S1. The ZPE and TS values (in eV) for gaseous molecules at 298 K.

Adsorbates	$Fe@C_6N_6$		$Co@C_6N_6$		$Ni@C_6N_6$	
	ZPE	TS	ZPE	TS	ZPE	TS
$*CO_2$	0.32	0.29	0.31	0.25	0.32	0.31
*COOH	0.60	0.27	0.61	0.27	0.60	0.30
*OCHO	0.59	0.27	0.61	0.23	0.59	0.30
*CO	0.20	0.17	0.20	0.16	0.20	0.17
*HCOOH	0.89	0.23	0.90	0.23	0.90	0.23
*CHO	0.55	0.08	0.46	0.21	0.55	0.09
*COH	0.46	0.22	0.47	0.20	-	-
*CHOH	0.78	0.19	0.78	0.21	0.78	0.14
$*CH_2O$	0.76	0.21	0.76	0.21	0.76	0.21
$*CH_3O$	1.07	0.23	1.08	0.22	1.07	0.23
$*CH_2OH$	1.08	0.22	1.08	0.24	1.08	0.11
*CH	0.33	0.09	0.26	0.10	0.32	0.12
$*CH_2$	0.60	0.12	0.61	0.11	0.73	0.04
$*CH_3$	0.93	0.14	0.93	0.15	0.92	0.19
*O	0.06	0.06	0.06	0.07	0.05	0.09
*OH	0.34	0.11	0.33	0.15	0.34	0.14
$*CH_3OH$	1.40	0.30	1.36	0.31	1.37	0.24
$*CH_4$	1.20	0.29	1.21	0.25	1.21	0.27

Table S2. The ZPE and TS values (in eV) for the adsorbates on $TM@C_6N_6$ systems (TM = Fe, Co, Ni).

Elementary steps	ΔG (eV)		
	$Fe@C_6N_6$	$Co@C_6N_6$	$Ni@C_6N_6$
1. $CO_2 + * \rightarrow *CO_2$	-0.09	-0.08	0.08
2. $*CO_2 + H^+ + e^- \rightarrow *COOH$	0.60	0.47	0.55
3. $*CO_2 + H^+ + e^- \rightarrow *OCHO$	-0.15	0.29	0.30
4. $*COOH + H^+ + e^- \rightarrow *CO + H_2O$	-0.70	-1.10	-1.00
5. $*CO \rightarrow CO + *$	0.83	1.35	1.01
6. $*COOH + H^+ + e^- \rightarrow *HCOOH$	-0.86	-0.56	-0.68
7. $*OCHO + H^+ + e^- \rightarrow *HCOOH$	-0.12	-0.38	-0.44
8. $*HCOOH \rightarrow HCOOH + *$	0.94	0.76	0.64
9. $*CO + H^+ + e^- \rightarrow *CHO$	0.26	0.88	0.65
10. $*CO + H^+ + e^- \rightarrow *COH$	1.54	1.99	-
12. $*HCOOH + H^+ + e^- \rightarrow *CHO + H_2O$	0.43	0.34	0.33
12. $*CHO + H^+ + e^- \rightarrow *CHOH$	0.84	0.48	0.36
13. $*CHO + H^+ + e^- \rightarrow *CH_2O$	0.05	0.04	0.16
14. $*COH + H^+ + e^- \rightarrow *C + H_2O$	0.88	1.26	-
15. $*C + H^+ + e^- \rightarrow *CH$	-0.61	-0.09	-1.18
16. $*CHOH + H^+ + e^- \rightarrow *CH_2OH$	-0.48	-0.34	-0.76
17. $*CHOH + H^+ + e^- \rightarrow *CH + H_2O$	0.71	1.80	1.64
18. $*CH_2O + H^+ + e^- \rightarrow *CH_2OH$	0.31	0.10	-0.56
19. $*CH_2O + H^+ + e^- \rightarrow *OCH_3$	-0.55	-0.12	-0.12
20. $*CH_2OH + H^+ + e^- \rightarrow CH_3OH + *$	-0.39	-0.26	0.16

21. $*OCH_3 + H^+ + e^- \rightarrow CH_3OH + *$	0.47	-0.04	-0.28
22. $*OCH_3 + H^+ + e^- \rightarrow *O + CH_4$	0.26	-1.85	0.49
23. $*CH + H^+ + e^- \rightarrow *CH_2$	-0.90	-1.82	-1.19
24. $*CH_2OH + H^+ + e^- \rightarrow *CH_2 + H_2O$	0.29	0.32	1.20
25. $*CH_2 + H^+ + e^- \rightarrow *CH_3$	-1.03	-1.23	-1.46
26. $*CH_3 + H^+ + e^- \rightarrow CH_4 + *$	-0.84	-0.56	-0.79
27. $*O + H^+ + e^- \rightarrow *OH$	-1.21	-1.24	-1.61
28. $*OH + H^+ + e^- \rightarrow H_2O + *$	0.22	1.85	-0.36

Table S3. The Free energy changes (in eV) for the proposed elementary steps for CO_2RR pathways on $TM@C_6N_6$ systems (TM = Fe, Co, Ni).

		$Fe@C_6N_6$	$Co@C_6N_6$	$Ni@C_6N_6$
HER		0.40	0.38	0.61
CO_2RR	*COOH	0.60	0.47	0.55
	*OCHO	-0.15	0.29	0.30

Table S4. Free energy change (in eV) of HER and CO_2RR on $TM@C_6N_6$ systems (TM = Fe, Co, Ni).

Products		$Fe@C_6N_6$	$Co@C_6N_6$	$Ni@C_6N_6$
CO	PDS	*CO → CO + *		
	ΔG_{max}(eV)	0.83	1.35	1.01
HCOOH	PDS	*HCOOH → HCOOH + *		
	ΔG_{max}(eV)	0.94	0.76	0.64
CH_3OH	PDS	*HCOOH + H^+ + e^- → *CHO + H_2O		
	ΔG_{max}(eV)	0.43	0.34	0.33
CH_4	PDS	*HCOOH + H^+ + e^- → *CHO + H_2O		*OCH_3 + H^+ + e^- → *O + CH_4
	ΔG_{max}(eV)	0.43	0.34	0.49

Table S5. The maximum Gibbs Free energy values (in eV) of the potential determining steps for various C_1 products on $TM@C_6N_6$ systems (TM = Fe, Co, Ni).