

Table S1. The adsorption energy (eV) of different reaction species in Ni₄/Al₂O₃(110)

	Ni ₄ cluster	Interfacial site	Substrate
CH ₄	-0.34	-0.33	-0.03
CO ₂	-0.99	—	-0.50
H ₂ O	-0.78	-0.70	-0.66
CH	-7.86	-5.28	—
C	-7.44	-7.74	-5.21
CO	-2.90	—	-1.94
H ₂	-0.57	-0.44	-0.24
O	-4.70	—	-8.85
H	-2.86	—	-1.14
OH	-3.81	-3.13	-4.60

Table S2. The adsorption energy (eV) of different reaction species in Ni₄/ZrO₂(111)

	Ni ₄ cluster	Interfacial site	Substrate
CH ₄	-0.41	-0.02	-0.01
CO ₂	-0.93	—	-0.17
H ₂ O	-0.80	-0.49	-0.81
CO	-2.83	—	-1.35
H ₂	-0.63	-0.20	-0.02
CH	-6.31	-4.80	-2.91
C	-6.62	-3.77	-2.18
O	-5.98	—	-6.02
H	-2.76	-2.49	-1.82
OH	-3.96	-4.39	-4.42

Table S3. The adsorption energy (eV) of different reaction species in Ni₄/MgO(100)

	Ni ₄ cluster	Interfacial site	Substrate
CH ₄	-0.27	—	-0.28
CO ₂	-1.59	-0.90	-0.14
H ₂ O	-0.49	—	-0.63
CO	-3.29	-3.25	-1.11
H ₂	-0.65	—	-0.35
CH	-6.62	-4.81	-1.65
C	-8.16	-5.12	—
O	-6.19	-5.85	—
H	-2.96	-2.67	-0.61
OH	-4.26	-4.69	—

Table S4. The adsorption energy (eV) of different reaction species in Ni₄/SiO₂(110)

	Site	E _{ads}	Site	E _{ads}	Site	E _{ads}
CH ₄	Si	-0.03	Si-Ni	-0.10	Si-Ni	-0.08
CO ₂	Si	-0.14	Si	-0.15	Ni-N	-0.10
H ₂ O	Ni	-0.43	Ni	-0.73	Ni	-1.10
CO	Ni	-2.08	Ni	-1.99	Si-Ni	-2.13
H ₂	Ni	-0.14	Ni-Si	-0.04	Si	-0.13
CH	O	-5.76	O	-4.71	Ni-Ni	-1.67
C	O	-6.03	O	-6.69	—	—
O	Ni	-3.41	Ni-Ni	-3.75	—	—
H	O	-3.13	Ni	-2.07	Ni	-1.76
OH	Ni	-2.75	Ni	-2.65	Ni-Ni	-2.55

Table S5. The adsorption energies of all reaction species on Ni(111) surface (eV)

Adsorption energy		Adsorption energy	
CH ₄	-0.33	CH	-6.76
CO ₂	-0.36	C	-7.11
H ₂ O	-0.66	O	-5.95
CO	-2.17	H	-3.07
H ₂	-0.25	OH	-3.74

Table S6. The most stable adsorption of all reaction species on different catalysts

	Ni ₄ /Al ₂ O ₃ (110)	E _{ads} (eV)	Ni ₄ /ZrO ₂ (111)	E _{ads} (eV)	Ni ₄ /MgO(100)	E _{ads} (eV)	Ni ₄ /SiO ₂ (110)	E _{ads} (eV)
CH ₄	Ni ₄ cluster	-0.34	Ni ₄ cluster	-0.41	substrate	-0.28	Ni	-0.10
CO ₂	Ni ₄ cluster	-0.99	Ni ₄ cluster	-0.93	Ni ₄ cluster	-1.59	\	-0.15
H ₂ O	Ni ₄ cluster	-0.78	substrate	-0.81	substrate	-0.63	Ni	-1.10
CO	Ni ₄ cluster	-2.90	Ni ₄ cluster	-2.83	Ni ₄ cluster	-3.29	Ni	-2.13
H ₂	Ni ₄ cluster	-0.57	Ni ₄ cluster	-0.63	Ni ₄ cluster	-0.57	Ni	-0.14
CH	Ni ₄ cluster	-7.86	Ni ₄ cluster	-6.31	Ni ₄ cluster	-6.62	O-Ni	-5.76
C	Ni ₄ cluster	-7.74	Ni ₄ cluster	-6.62	Ni ₄ cluster	-8.16	O-Ni	-6.69
O	substrate	-8.85	substrate	-6.02	Ni ₄ cluster	-6.19	Ni-Ni	-3.75
H	Ni ₄ cluster	-2.86	Ni ₄ cluster	-2.76	Ni ₄ cluster	-2.96	O	-3.13
OH	substrate	-4.60	substrate	-4.42	Interface	-4.69	Ni	-2.75

Table S7. The adsorption strength order of different species

The adsorption strength order					
	1 ^a	2	3	4	5
CH ₄	Ni ₄ /ZrO ₂ (111)	Ni ₄ /Al ₂ O ₃ (110)	Ni(111)	Ni ₄ /MgO(100)	Ni ₄ /SiO ₂ (110)
CO ₂	Ni ₄ /MgO(100)	Ni ₄ /Al ₂ O ₃ (110)	Ni/ZrO ₂ (111)	Ni(111)	Ni ₄ /SiO ₂ (110)
H ₂ O	Ni ₄ /SiO ₂ (110)	Ni/ZrO ₂ (111)	Ni ₄ /Al ₂ O ₃ (110)	Ni(111)	Ni ₄ /MgO(100)
CO	Ni ₄ /MgO(100)	Ni ₄ /Al ₂ O ₃ (110)	Ni/ZrO ₂ (111)	Ni(111)	Ni ₄ /SiO ₂ (110)
H ₂	Ni/ZrO ₂ (111)	Ni ₄ /MgO(100)	Ni ₄ /Al ₂ O ₃ (110)	Ni(111)	Ni ₄ /SiO ₂ (110)
CH	Ni ₄ /Al ₂ O ₃ (110)	Ni(111)	Ni ₄ /MgO(100)	Ni/ZrO ₂ (111)	Ni ₄ /SiO ₂ (110)
C	Ni ₄ /MgO(100)	Ni ₄ /Al ₂ O ₃ (110)	Ni(111)	Ni ₄ /SiO ₂ (110)	Ni/ZrO ₂ (111)
O	Ni ₄ /Al ₂ O ₃ (110)	Ni ₄ /MgO(100)	Ni/ZrO ₂ (111)	Ni(111)	Ni ₄ /SiO ₂ (110)
H	Ni ₄ /SiO ₂ (110)	Ni(111)	Ni ₄ /MgO(100)	Ni ₄ /Al ₂ O ₃ (110)	Ni/ZrO ₂ (111)
OH	Ni ₄ /MgO(100)	Ni ₄ /Al ₂ O ₃ (110)	Ni/ZrO ₂ (111)	Ni(111)	Ni ₄ /SiO ₂ (110)

^a The sequence from 1 to 5 indicates the adsorption from strong to weak

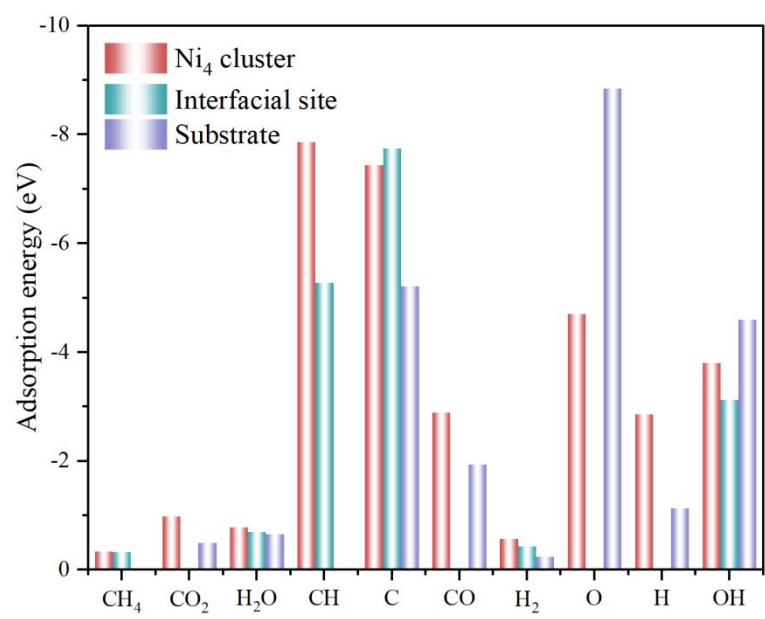


Figure S1. The adsorption energy (eV) of reaction species in Ni₄/Al₂O₃(110).

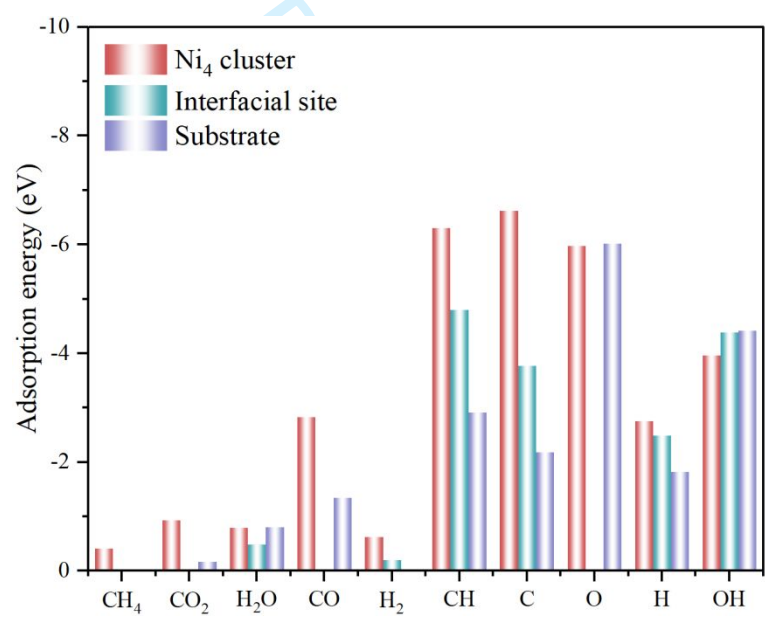


Figure S2. The adsorption energy (eV) of reaction species in Ni₄/ZrO₂(111).

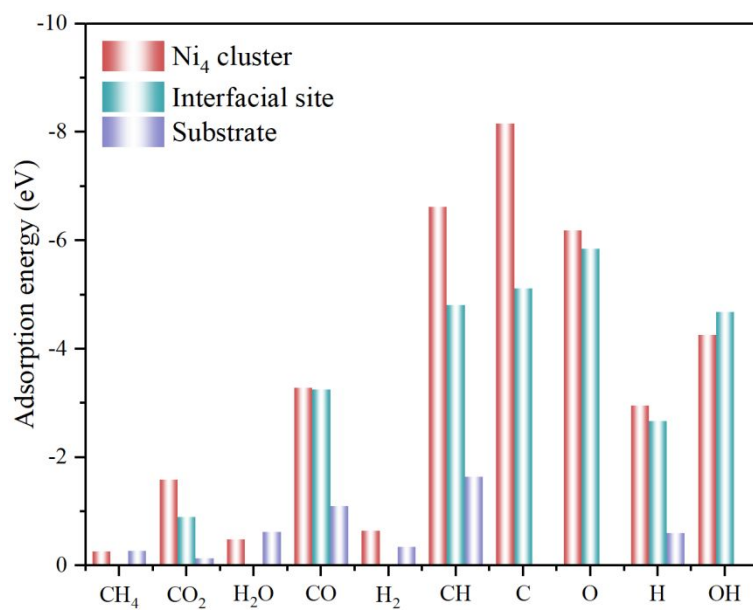


Figure S3. The adsorption energy (eV) of reaction species in Ni₄/MgO(100).

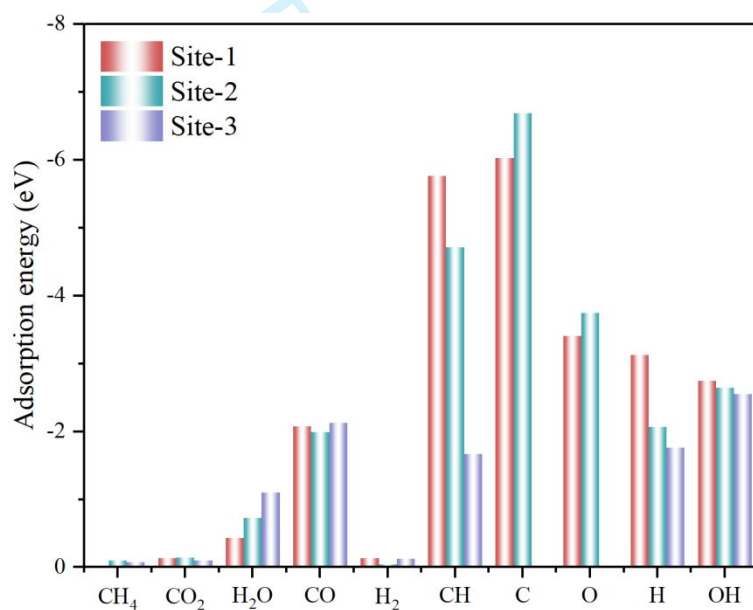


Figure S4. The adsorption energy (eV) of reaction species in Ni₄/SiO₂(110).

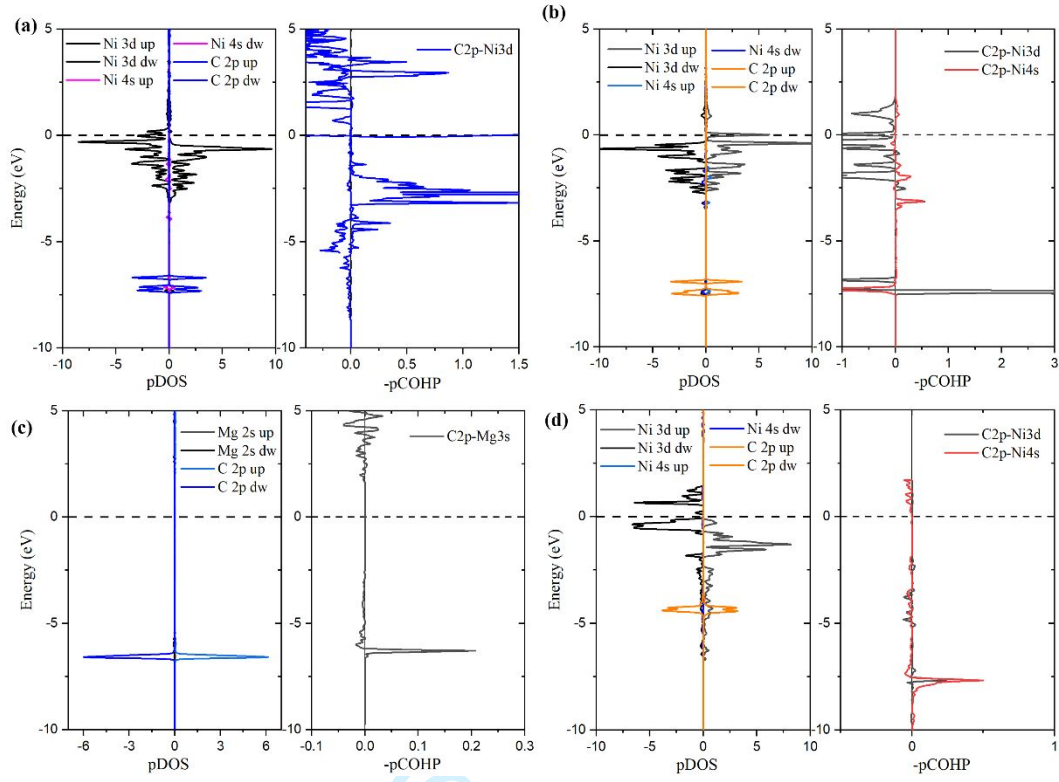


Figure S5. DOS and COHP diagrams for CH₄ adsorption on (a) Ni₄/Al₂O₃(110), (b) Ni₄/ZrO₂(111), (c) Ni₄/MgO(100), and (d) Ni₄/SiO₂(110).

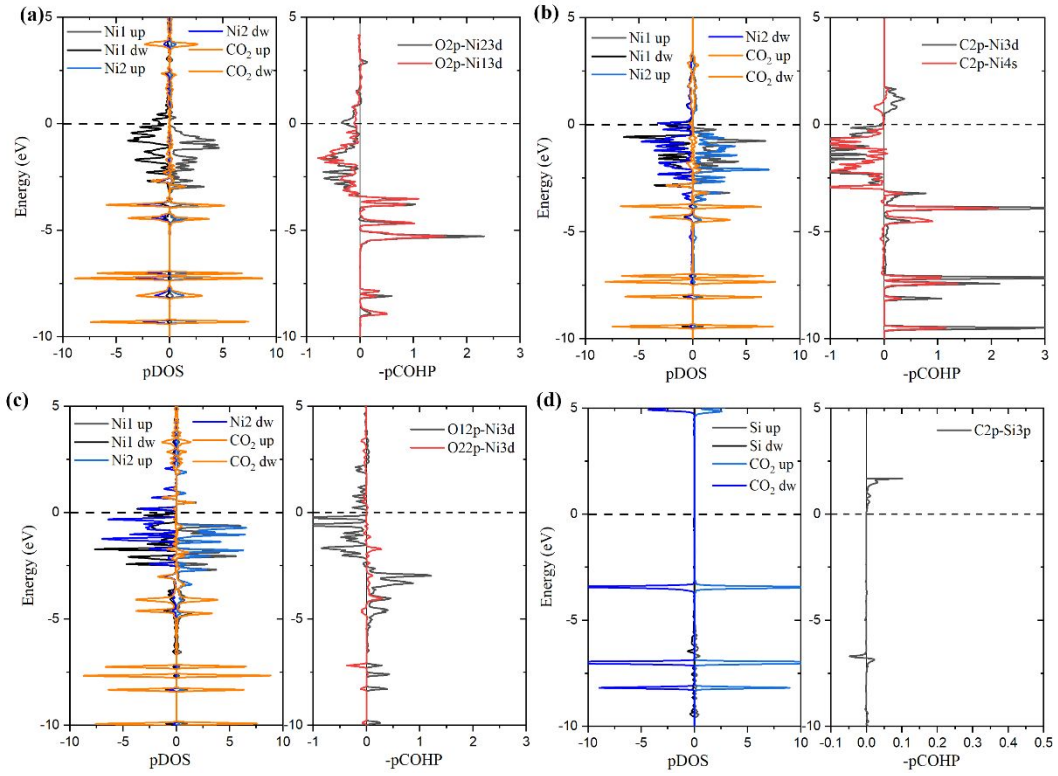


Figure S6. DOS and COHP diagrams for CO₂ adsorption on (a) Ni₄/Al₂O₃(110), (b) Ni₄/ZrO₂(111), (c) Ni₄/MgO(100), and (d) Ni₄/SiO₂(110).

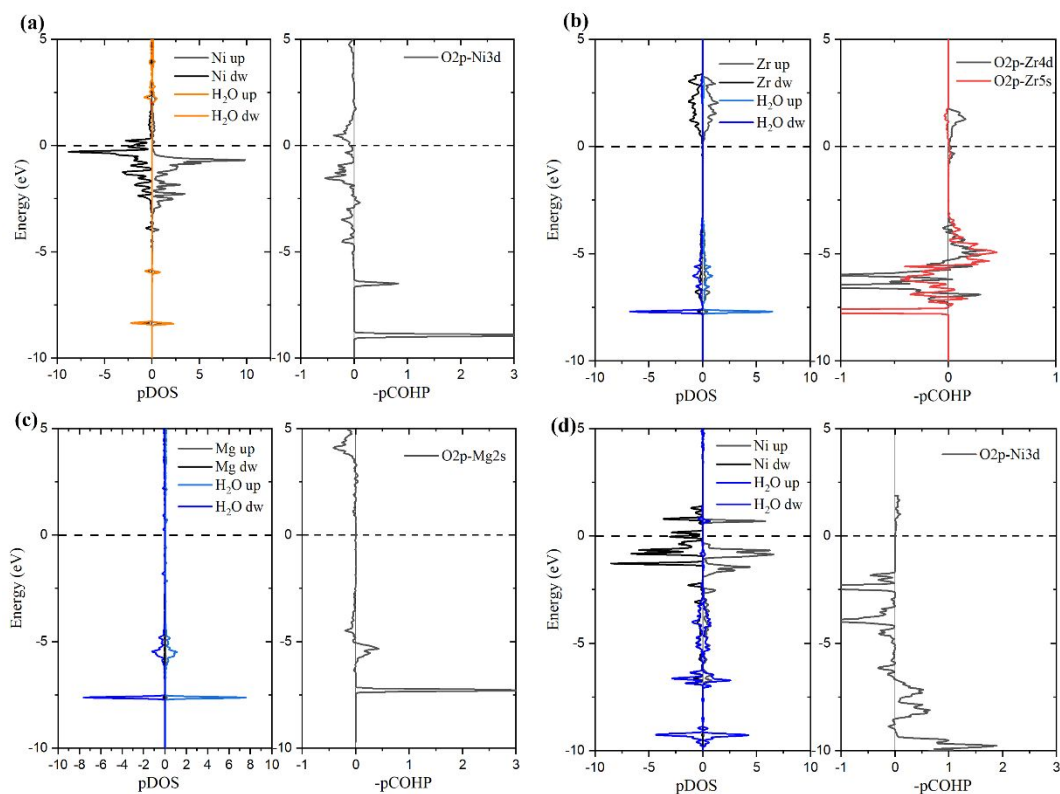


Figure S7. DOS and COHP diagrams for H₂O adsorption on (a) Ni₄/Al₂O₃(110), (b) Ni₄/ZrO₂(111), (c) Ni₄/MgO(100), and (d) Ni₄/SiO₂(110).

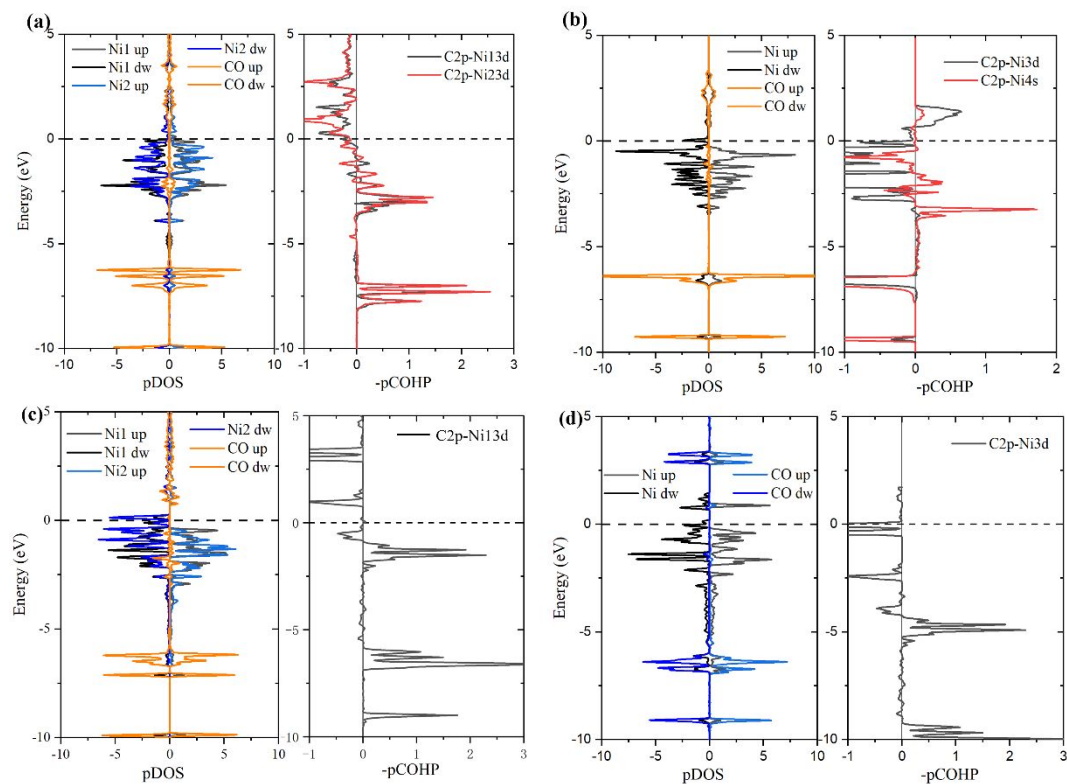


Figure S8. DOS and COHP diagrams for CO adsorption on (a) Ni₄/Al₂O₃(110), (b)

Ni₄/ZrO₂(111), (c) Ni₄/MgO(100), and (d) Ni₄/SiO₂(110).

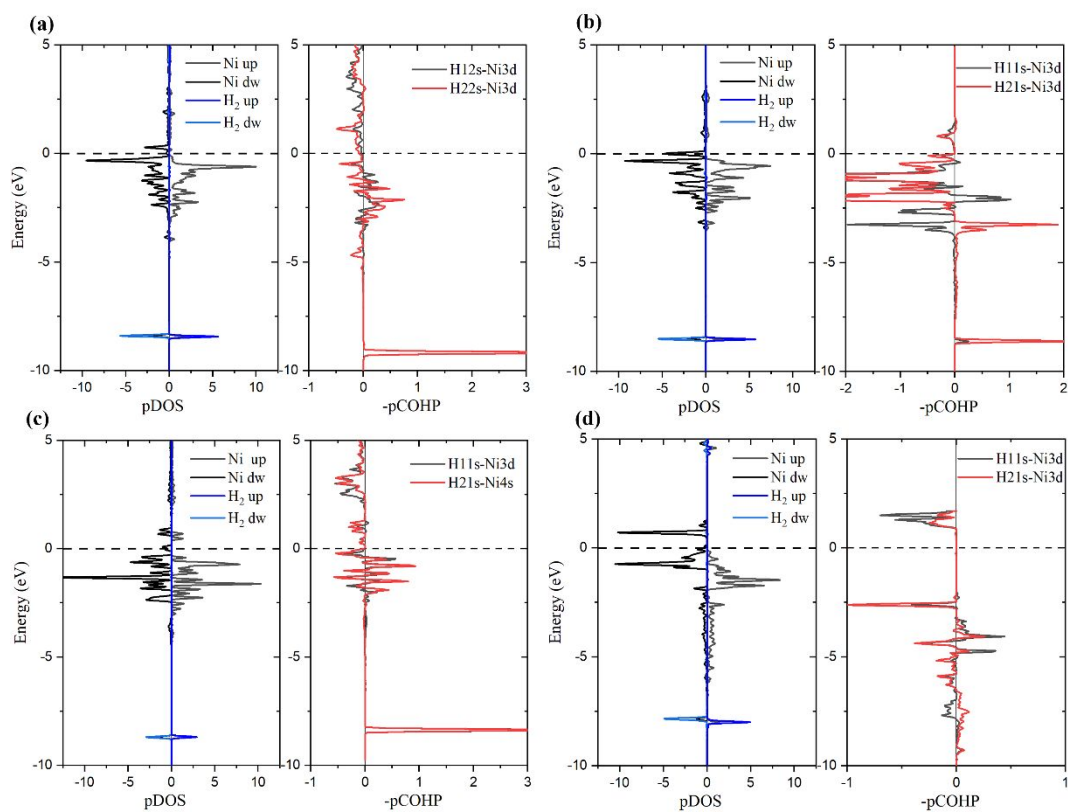


Figure S9. DOS and COHP diagrams for H₂ adsorption on (a) Ni₄/Al₂O₃(110), (b) Ni₄/ZrO₂(111), (c) Ni₄/MgO(100), and (d) Ni₄/SiO₂(110).

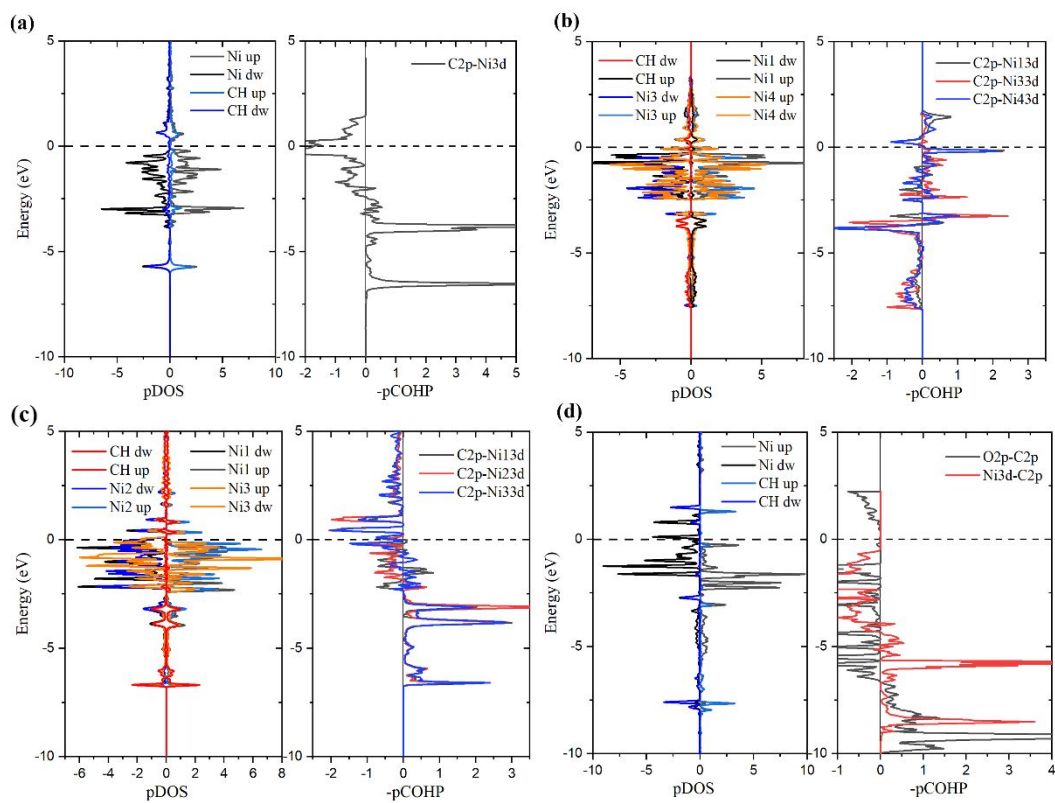


Figure S10. DOS and COHP diagrams for CH adsorption on (a) $\text{Ni}_4/\text{Al}_2\text{O}_3(110)$, (b) $\text{Ni}_4/\text{ZrO}_2(111)$, (c) $\text{Ni}_4/\text{MgO}(100)$, and (d) $\text{Ni}_4/\text{SiO}_2(110)$.

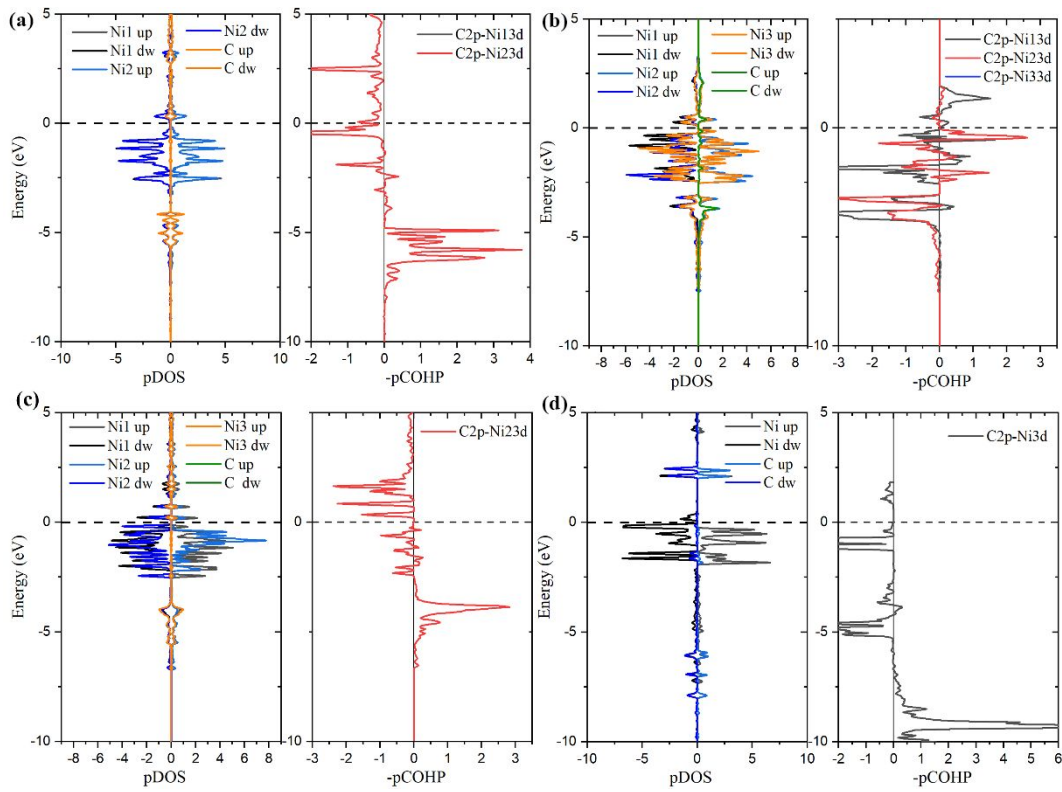


Figure S11. DOS and COHP diagrams for C adsorption on (a) $\text{Ni}_4/\text{Al}_2\text{O}_3(110)$, (b) $\text{Ni}_4/\text{ZrO}_2(111)$, (c) $\text{Ni}_4/\text{MgO}(100)$, and (d) $\text{Ni}_4/\text{SiO}_2(110)$.

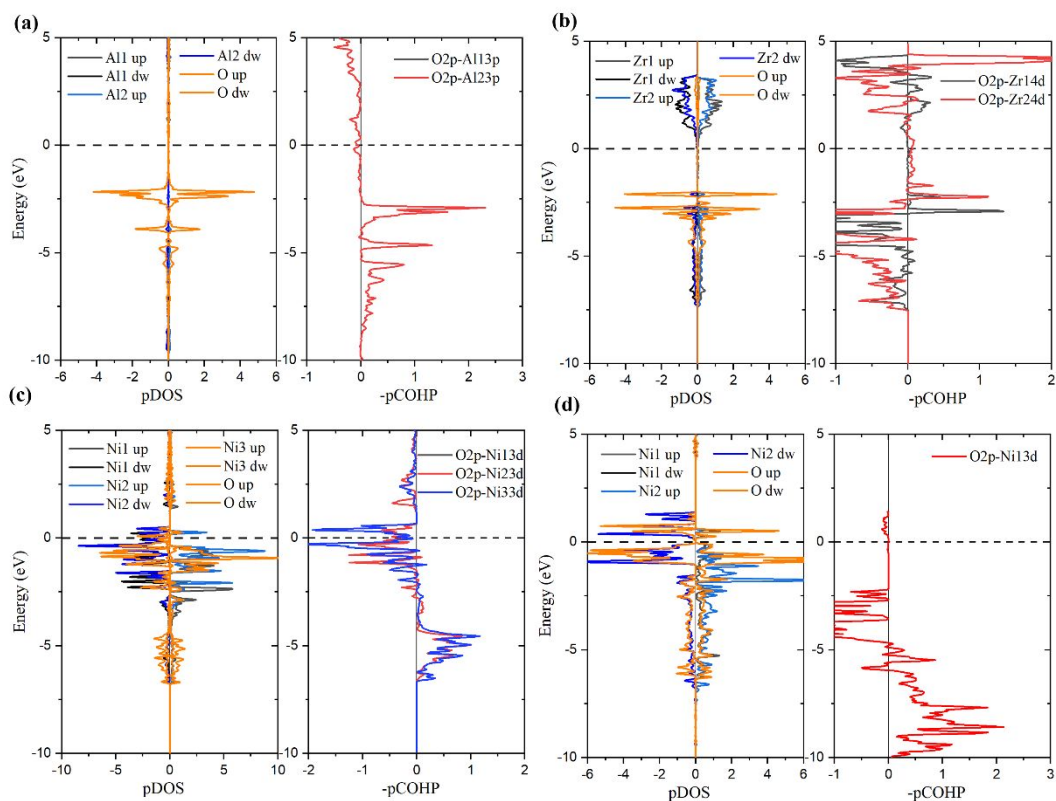


Figure S12. DOS and COHP diagrams for O adsorption on (a) $\text{Ni}_4/\text{Al}_2\text{O}_3(110)$, (b) $\text{Ni}_4/\text{ZrO}_2(111)$, (c) $\text{Ni}_4/\text{MgO}(100)$, and (d) $\text{Ni}_4/\text{SiO}_2(110)$.

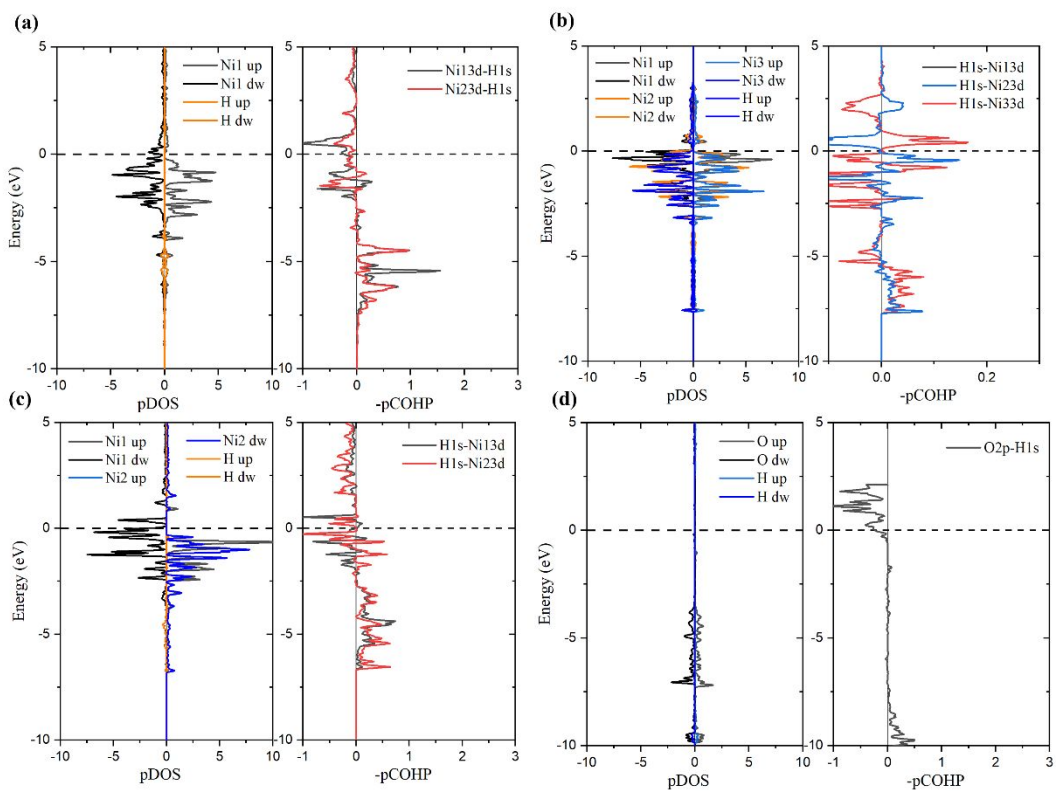


Figure S13. DOS and COHP diagrams for H adsorption on (a) $\text{Ni}_4/\text{Al}_2\text{O}_3(110)$, (b) $\text{Ni}_4/\text{ZrO}_2(111)$, (c) $\text{Ni}_4/\text{MgO}(100)$, and (d) $\text{Ni}_4/\text{SiO}_2(110)$.

$\text{Ni}_4/\text{ZrO}_2(111)$, (c) $\text{Ni}_4/\text{MgO}(100)$, and (d) $\text{Ni}_4/\text{SiO}_2(110)$.

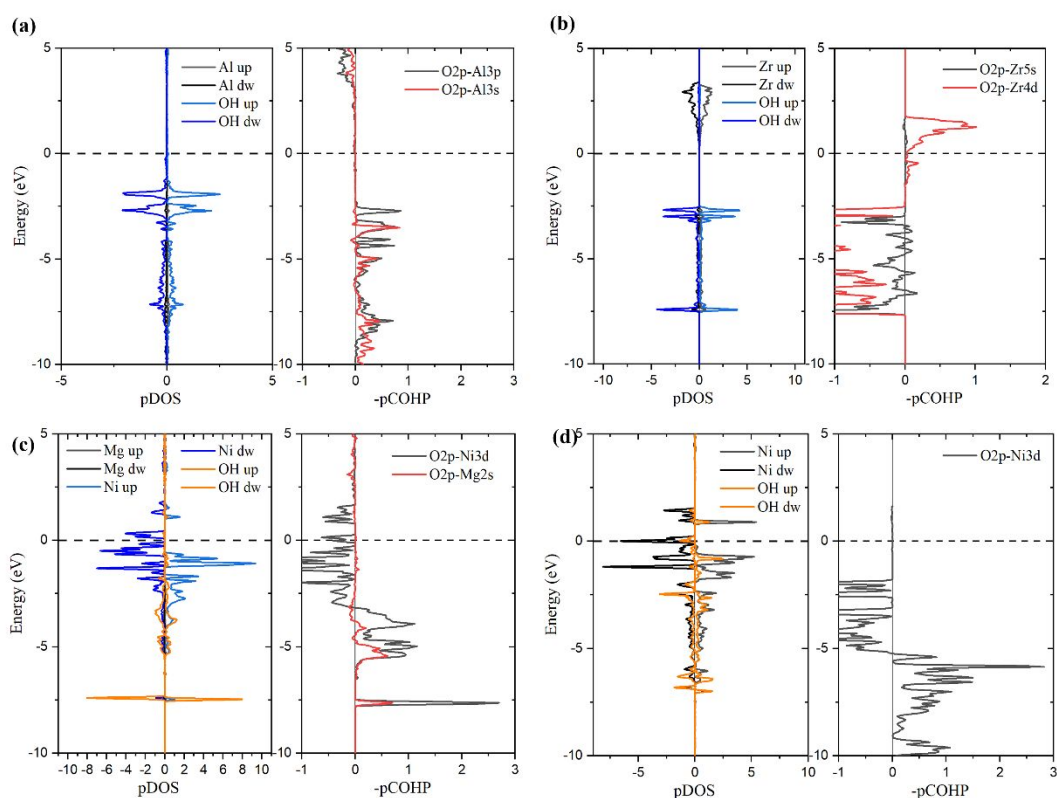


Figure S14, DOS and COHP diagrams for OH adsorption on (a) $\text{Ni}_4/\text{Al}_2\text{O}_3(110)$, (b) $\text{Ni}_4/\text{ZrO}_2(111)$, (c) $\text{Ni}_4/\text{MgO}(100)$, and (d) $\text{Ni}_4/\text{SiO}_2(110)$.

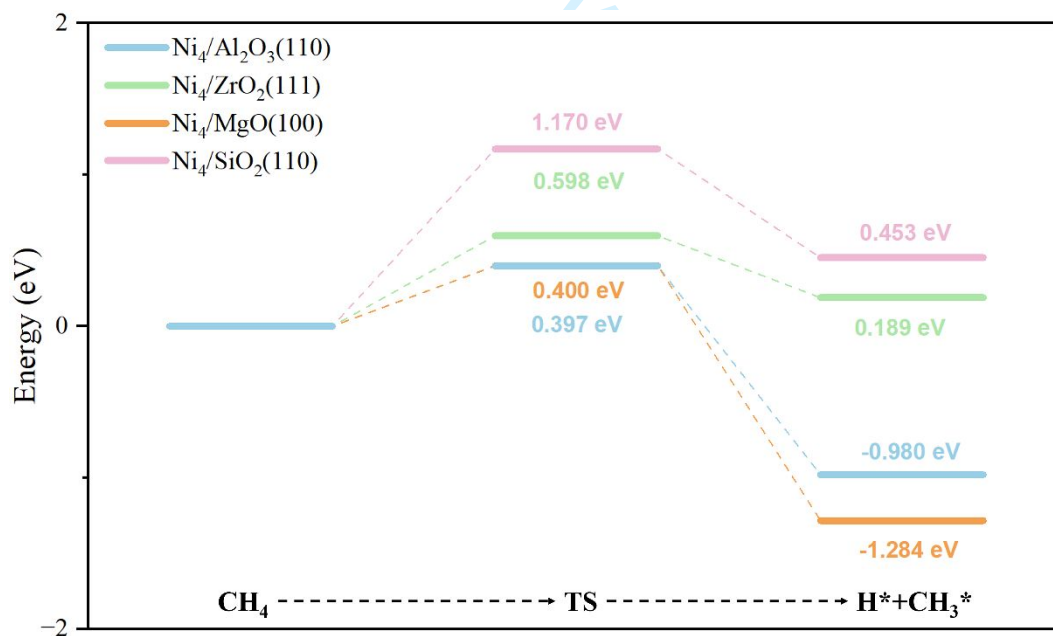


Figure S15. The energy diagram for C–H activation for CH_4 on different catalysts.