Electronic Supplementary Information

An atom-level insight into the oxide support effect of Ni-based catalysts on the syngas production in methane reforming

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S1 The adsorption energy of different reaction species on various catalysts

Table S1 The adsorption energy (eV) of different reaction species in $Ni_4/Al_2O_3(110)$

	Ni_4 cluster	Interfacial site	Substrate
CH_4	-0.34	-0.33	-0.03
CO_2	-0.99	—	-0.50
H_2O	-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

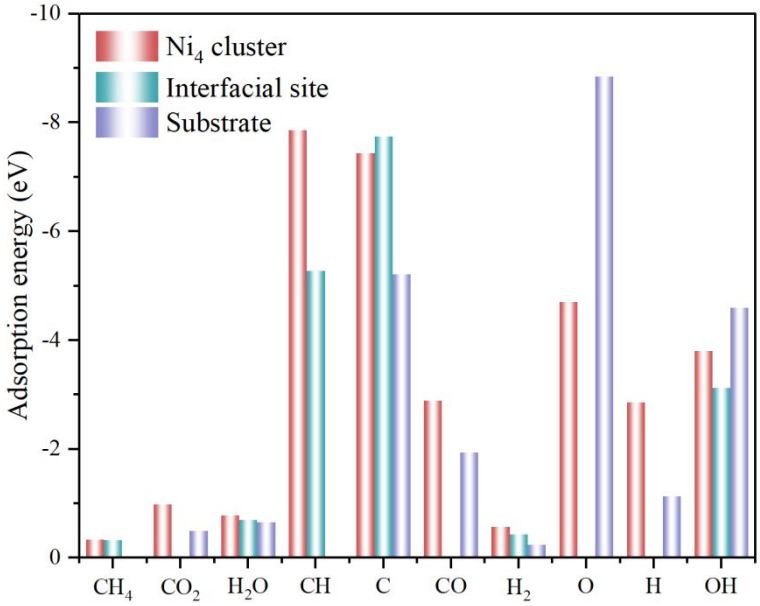

Fig. S1 The adsorption energy (eV) of reaction species in $Ni_4/Al_2O_3(110)$

Table S2 The adsorption energy (eV) of different reaction species in $Ni_4/ZrO_2(111)$

	Ni_4 cluster	Interfacial site	Substrate
CH_4	-0.41	-0.02	-0.01
CO_2	-0.93	—	-0.17
H_2O	-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

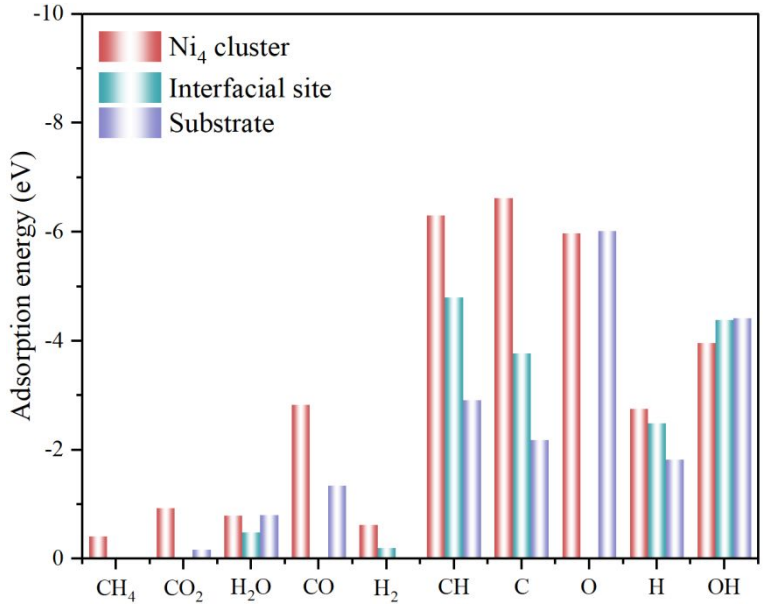

Fig. S2 The adsorption energy (eV) of reaction species in $Ni_4/ZrO_2(111)$

Table S3 The adsorption energy (eV) of different reaction species in $Ni_4/MgO(100)$

	Ni_4 cluster	Interfacial site	Substrate
CH_4	-0.27	—	-0.28
CO_2	-1.59	-0.90	-0.14
H_2O	-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	—

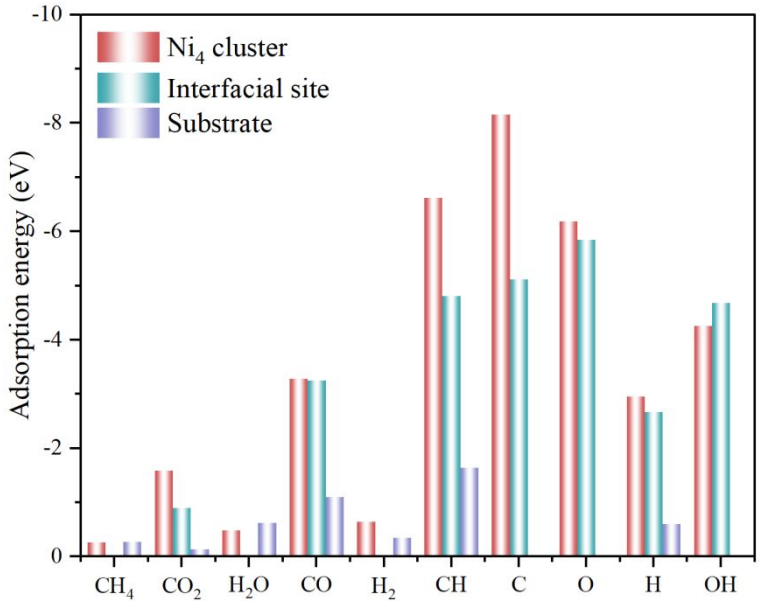

Fig. S3 The adsorption energy (eV) of reaction species in Ni_4/MgO(100)

Table S4 The adsorption energy (eV) of different reaction species in Ni_4/SiO_2(110)

	Site-1	E_{ads}	Site-2	E_{ads}	Site-3	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_2O	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

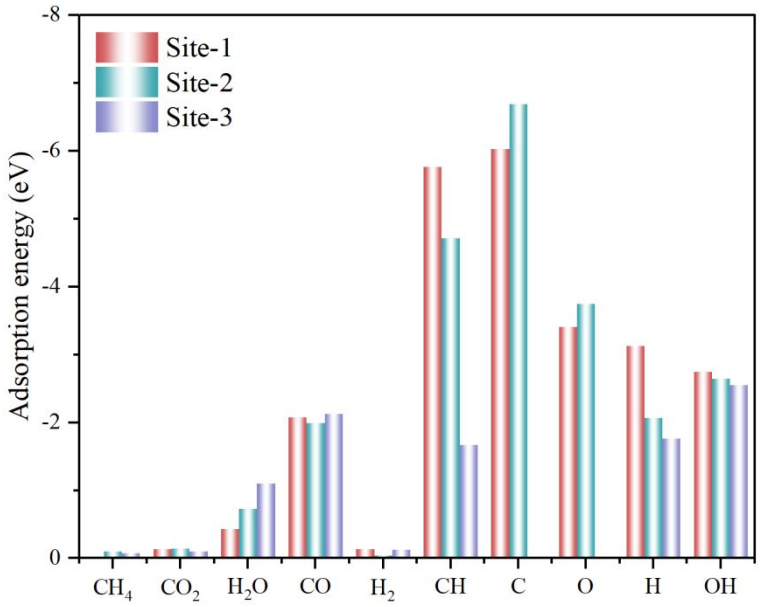

Fig. S4 The adsorption energy (eV) of reaction species in $Ni_4/SiO_2(110)$

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_2O	-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_2O_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_2O	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

S2 Density of state (DOS) and crystal orbital Hamilton population (COHP) diagrams

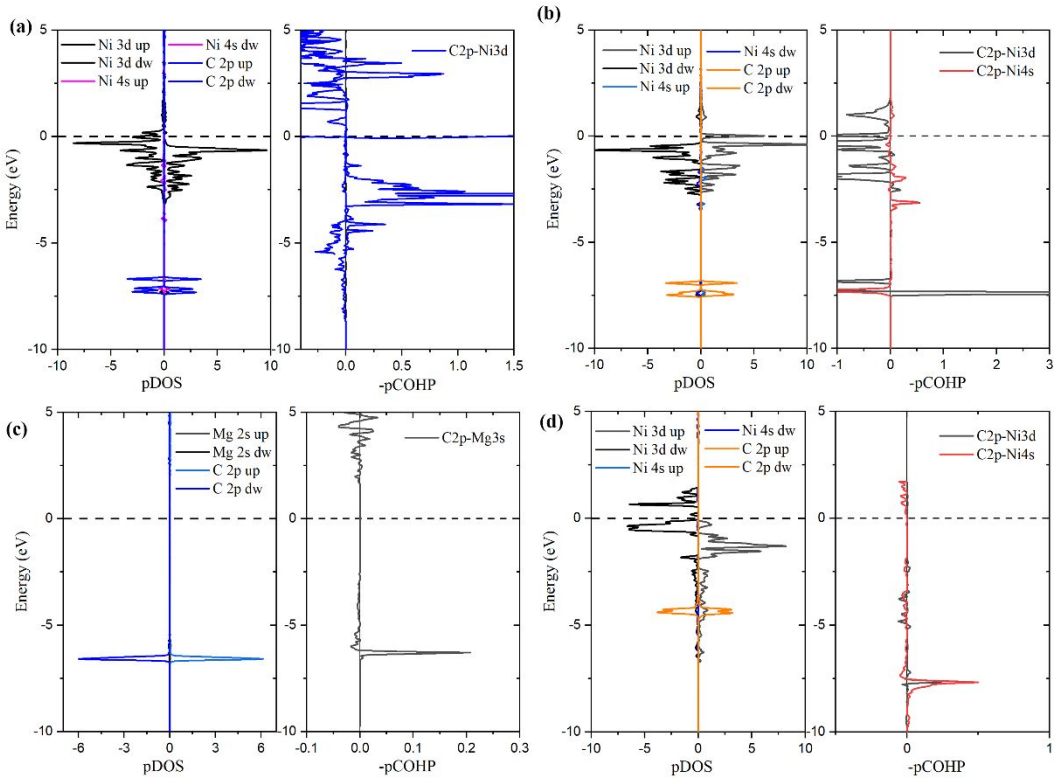

Fig. S5 DOS and COHP diagrams for CH_4 adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

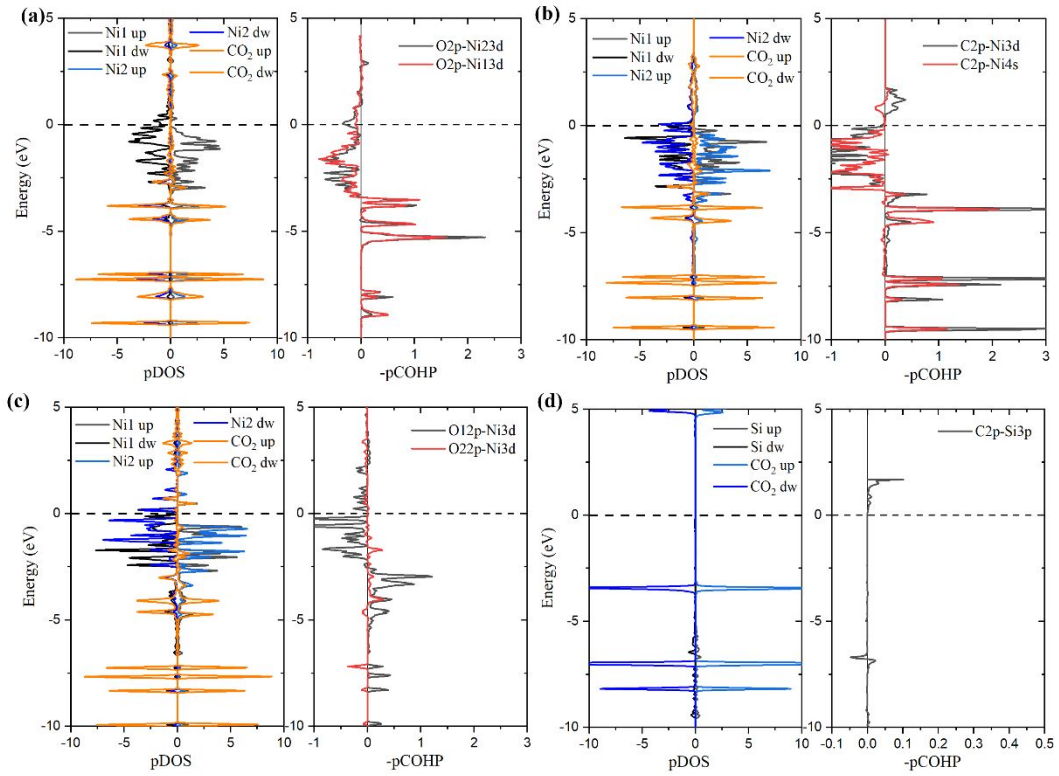

Fig. S6 DOS and COHP diagrams for CO_2 adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

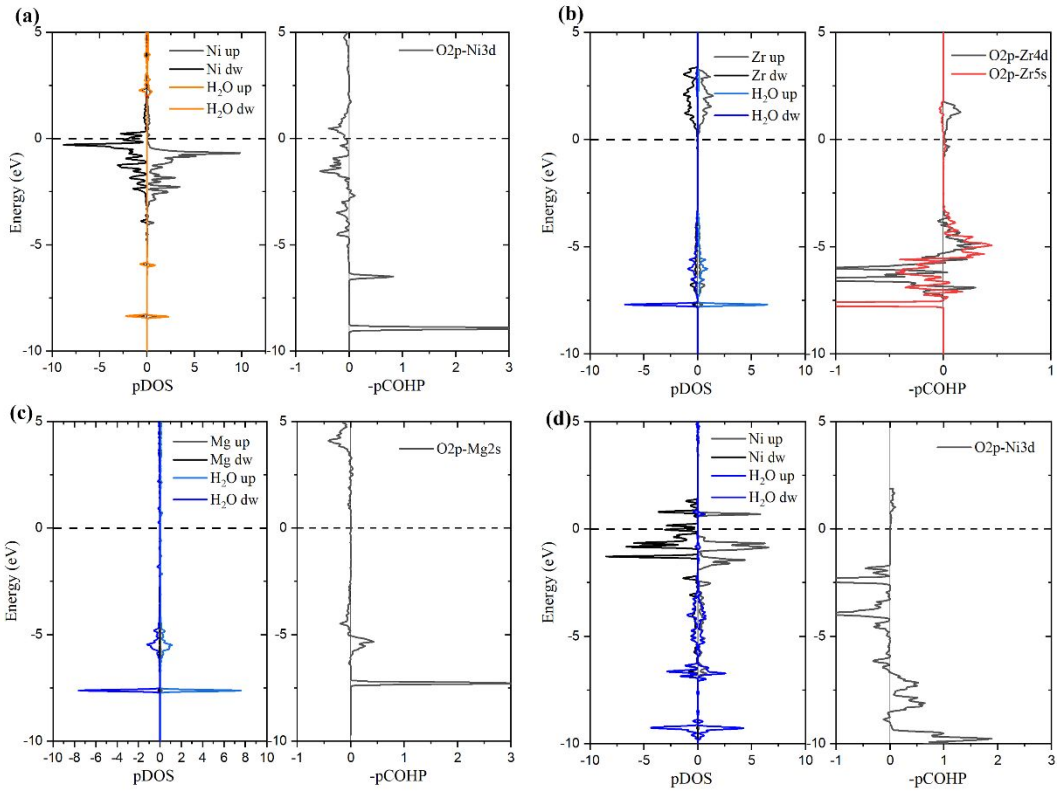

Fig. S7 DOS and COHP diagrams for H_2O adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

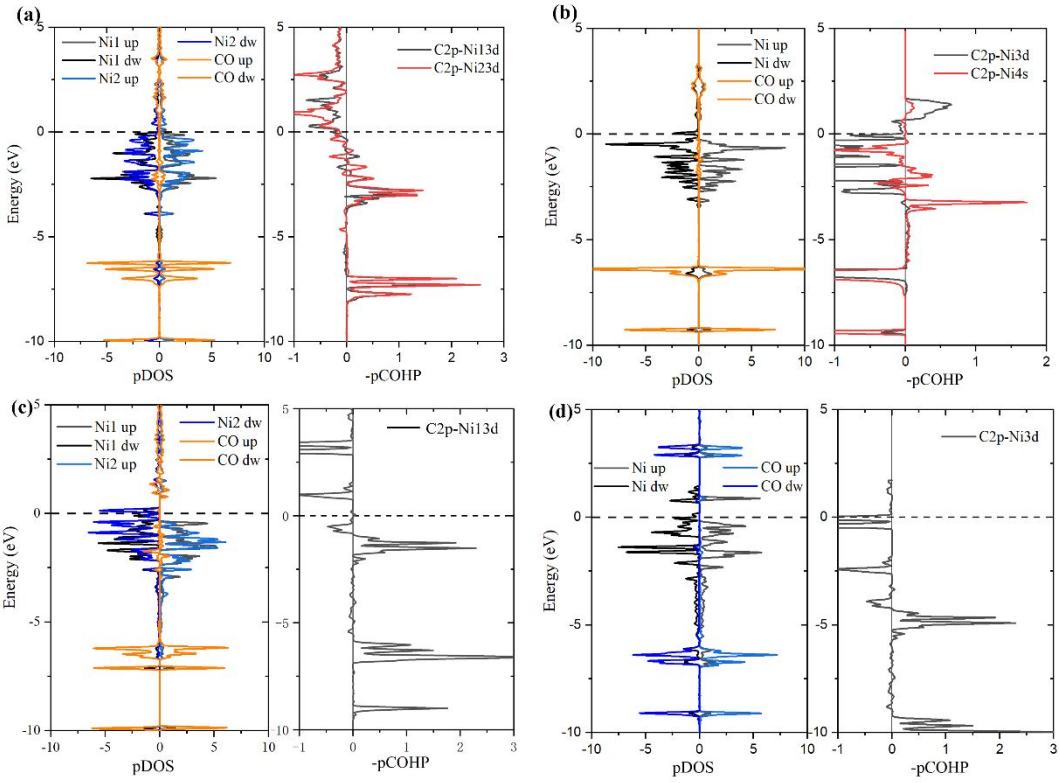

Fig. S8 DOS and COHP diagrams for CO adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

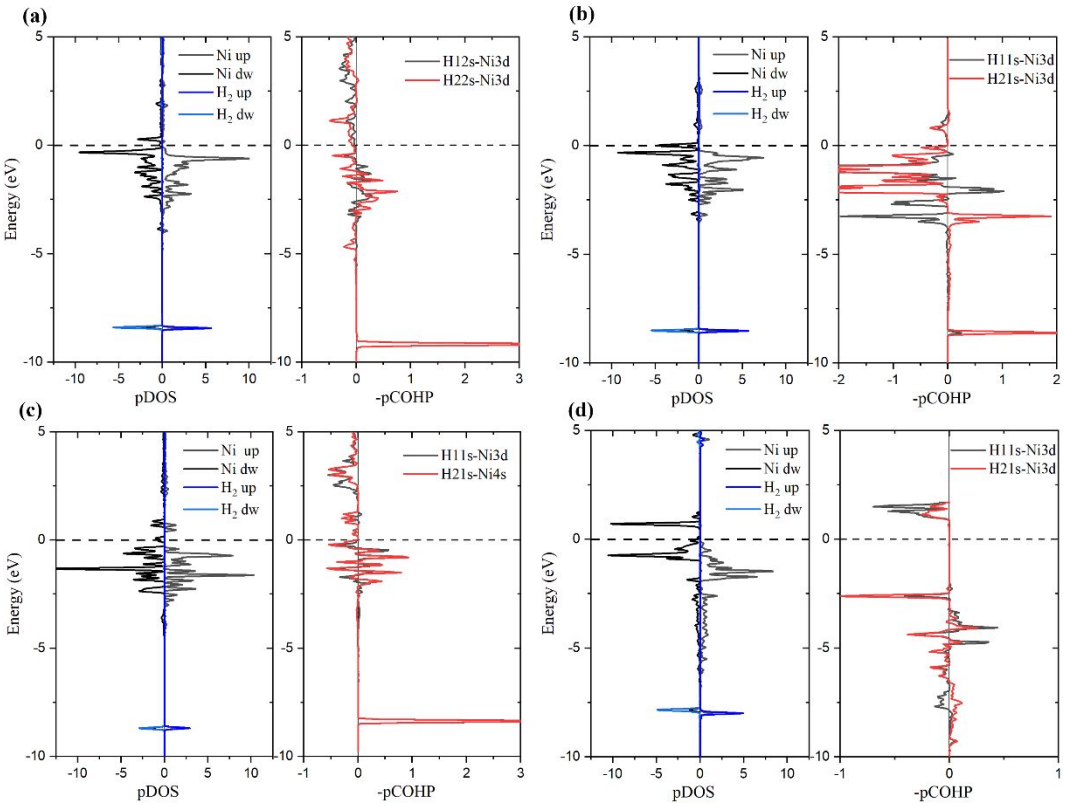

Fig. S9 DOS and COHP diagrams for H_2 adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

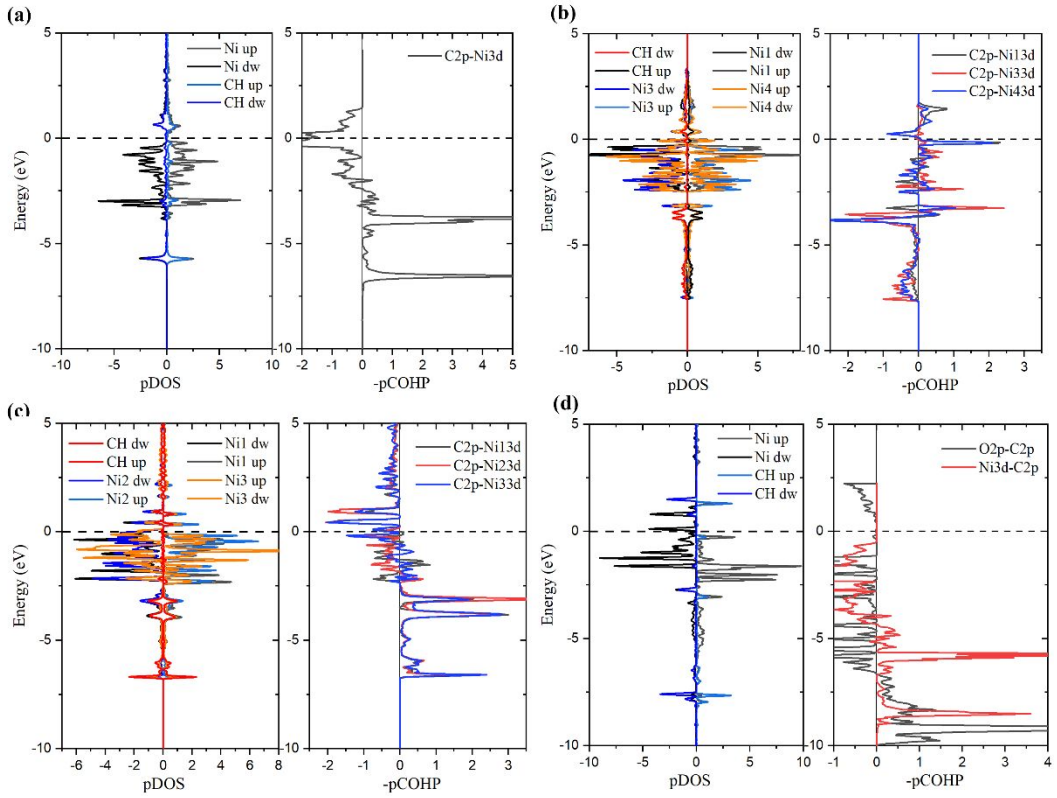

Fig. S10 DOS and COHP diagrams for CH adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

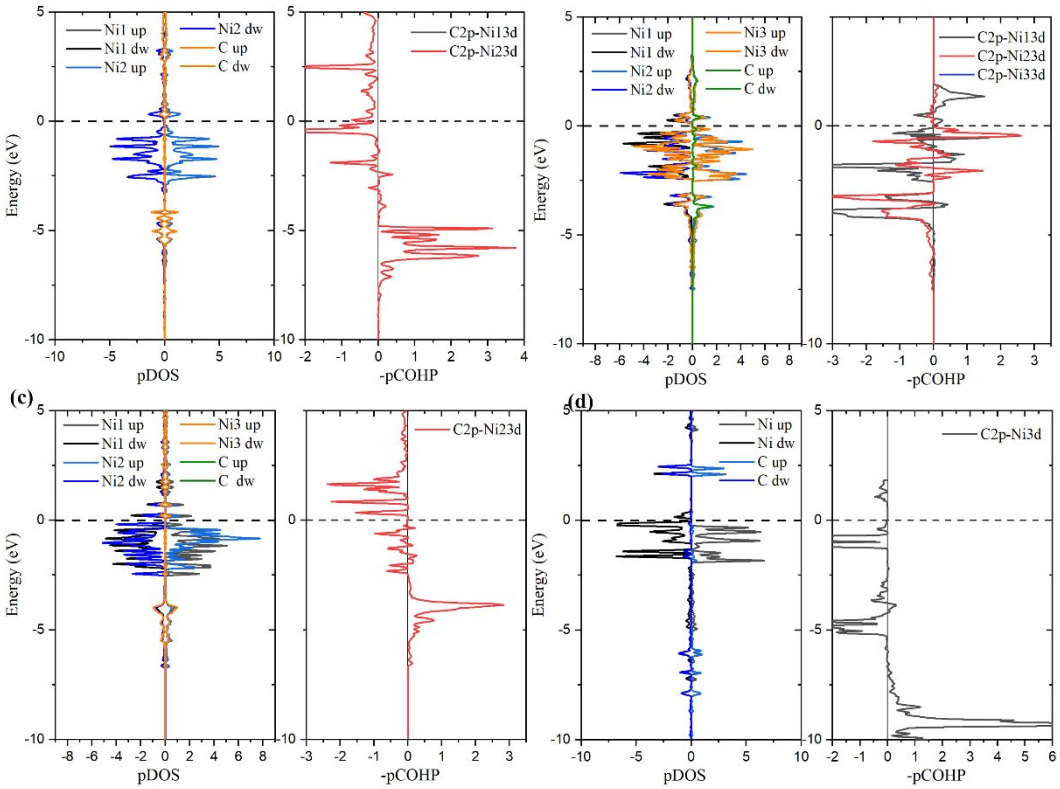

Fig. S11 DOS and COHP diagrams for C adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

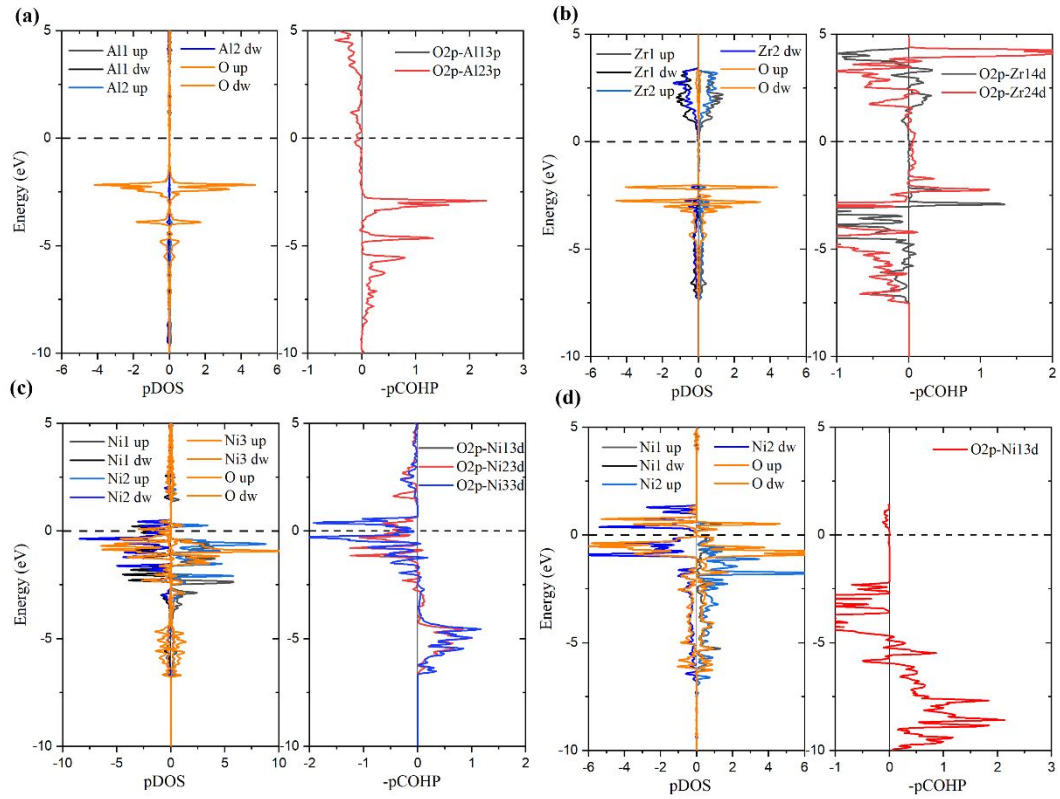

Fig. S12 DOS and COHP diagrams for O adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

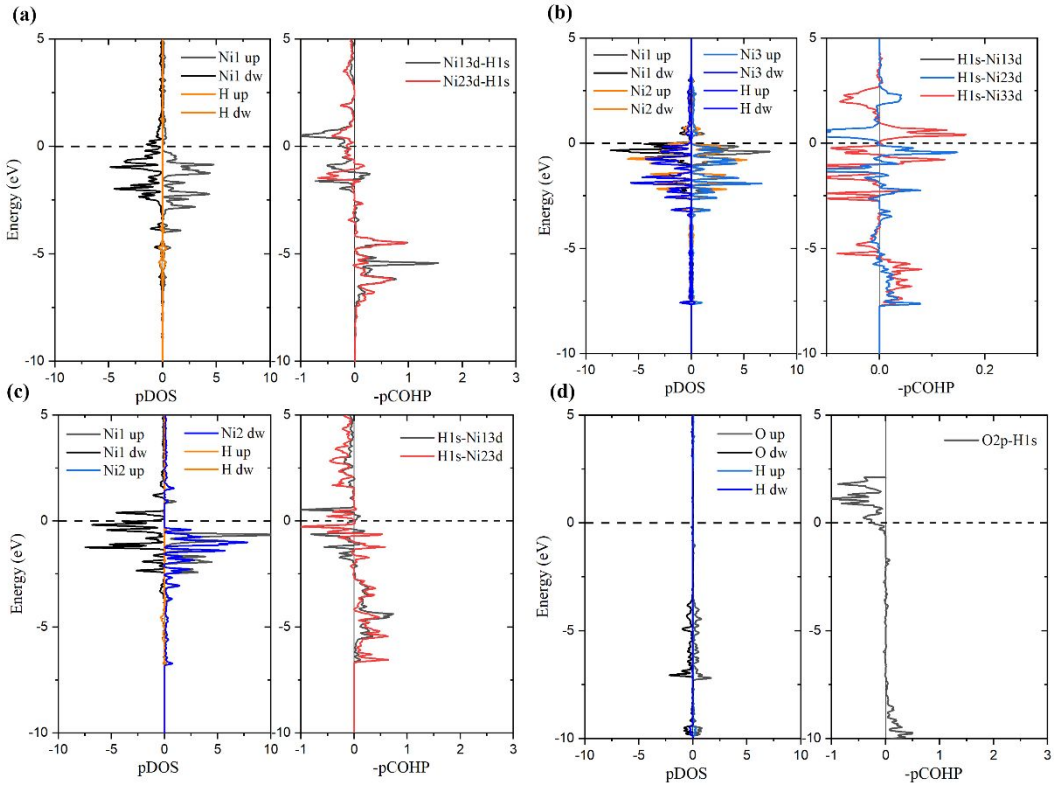

Fig. S13 DOS and COHP diagrams for H adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

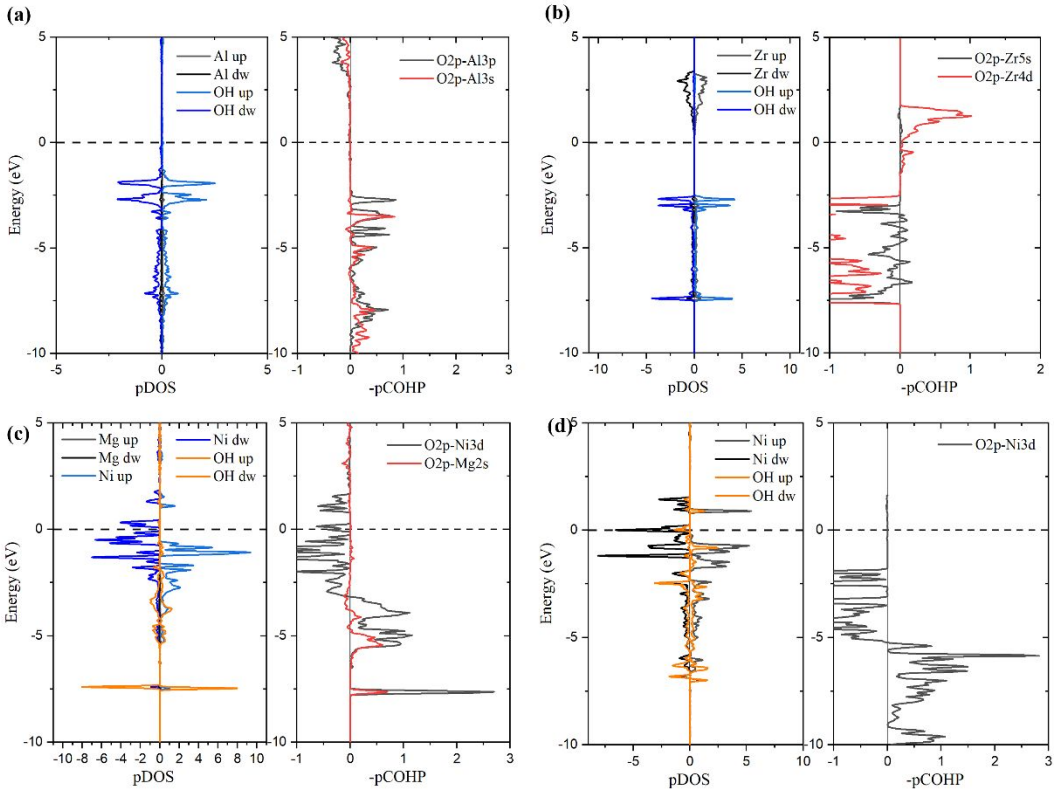

Fig. S14 DOS and COHP diagrams for OH adsorption on (a) $Ni_4/Al_2O_3(110)$, (b) $Ni_4/ZrO_2(111)$, (c) $Ni_4/MgO(100)$, and (d) $Ni_4/SiO_2(110)$

S3 The adsorption strength order of reaction species on different catalysts

Table S7 The adsorption strength order of different species

	The adsorption strength order				
	1[a]	2	3	4	5
CH_4	$Ni_4/ZrO_2(111)$	$Ni_4/Al_2O_3(110)$	Ni(111)	Ni_4/MgO(100)	$Ni_4/SiO_2(110)$
CO_2	Ni_4/MgO(100)	$Ni_4/Al_2O_3(110)$	$Ni/ZrO_2(111)$	Ni(111)	$Ni_4/SiO_2(110)$
H_2O	$Ni_4/SiO_2(110)$	$Ni/ZrO_2(111)$	$Ni_4/Al_2O_3(110)$	Ni(111)	Ni_4/MgO(100)
CO	Ni_4/MgO(100)	$Ni_4/Al_2O_3(110)$	$Ni/ZrO_2(111)$	Ni(111)	$Ni_4/SiO_2(110)$
H_2	$Ni/ZrO_2(111)$	Ni_4/MgO(100)	$Ni_4/Al_2O_3(110)$	Ni(111)	$Ni_4/SiO_2(110)$
CH	$Ni_4/Al_2O_3(110)$	Ni(111)	Ni_4/MgO(100)	$Ni/ZrO_2(111)$	$Ni_4/SiO_2(110)$
C	Ni_4/MgO(100)	$Ni_4/Al_2O_3(110)$	Ni(111)	$Ni_4/SiO_2(110)$	$Ni/ZrO_2(111)$
O	$Ni_4/Al_2O_3(110)$	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)	$Ni_4/Al_2O_3(110)$	$Ni/ZrO_2(111)$
OH	Ni_4/MgO(100)	$Ni_4/Al_2O_3(110)$	$Ni/ZrO_2(111)$	Ni(111)	$Ni_4/SiO_2(110)$

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

S4 The energy diagram for C–H activation for CH_4 on different catalysts

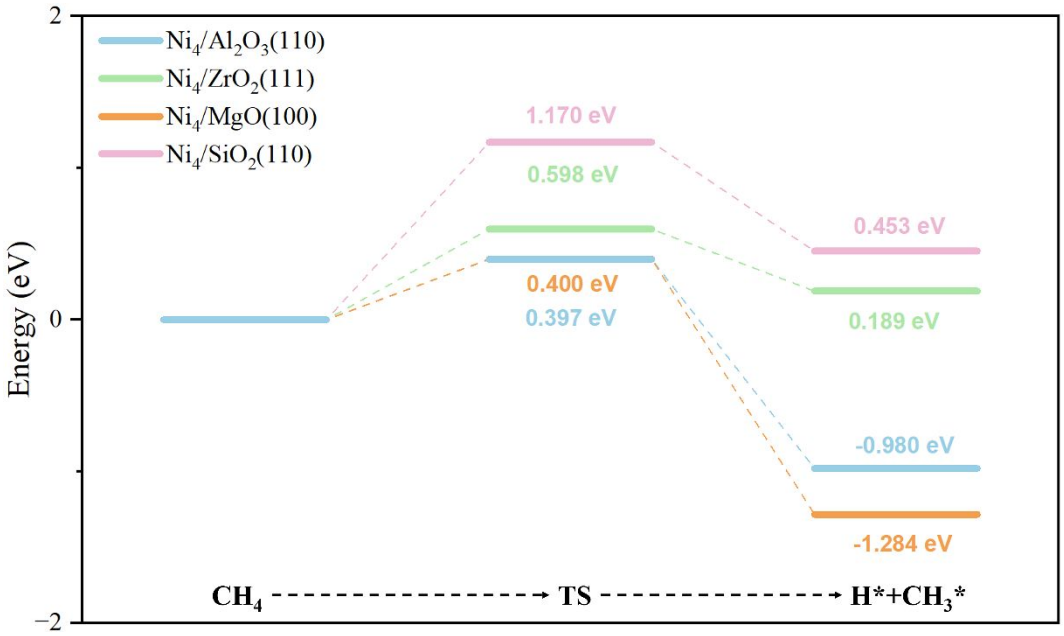

Fig. S15 The energy diagram for C–H activation for CH_4 on different catalysts