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RESEARCH ARTICLE

Pseudo-copper Ni-Zn alloy catalysts for carbon dioxide reduction to C_2 products

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SUPPLEMENTARY MATERIAL

Computational details

The adsorption energy (E_{ads}) of the intermediate on the catalysts was calculated by the following equation: $E_{ads} = E_{(sub+ads)} - E_{sub} - E_{ads}$, where $E_{(sub+ads)}$ is the total energy of the adsorbed intermediate on the substrate, E_{sub} is the energy of the substrate, and E_{ads} is the energy of the adsorbed intermediate.

The Gibbs free energy of each elementary step was calculated as: $\Delta G = \Delta E + \Delta ZPE - T*\Delta S$, where ΔE is the reaction energy calculated by the DFT. ΔZPE and ΔS are the changes in zero-point energy and entropy during the reaction, respectively. T is a constant (298.15 K).

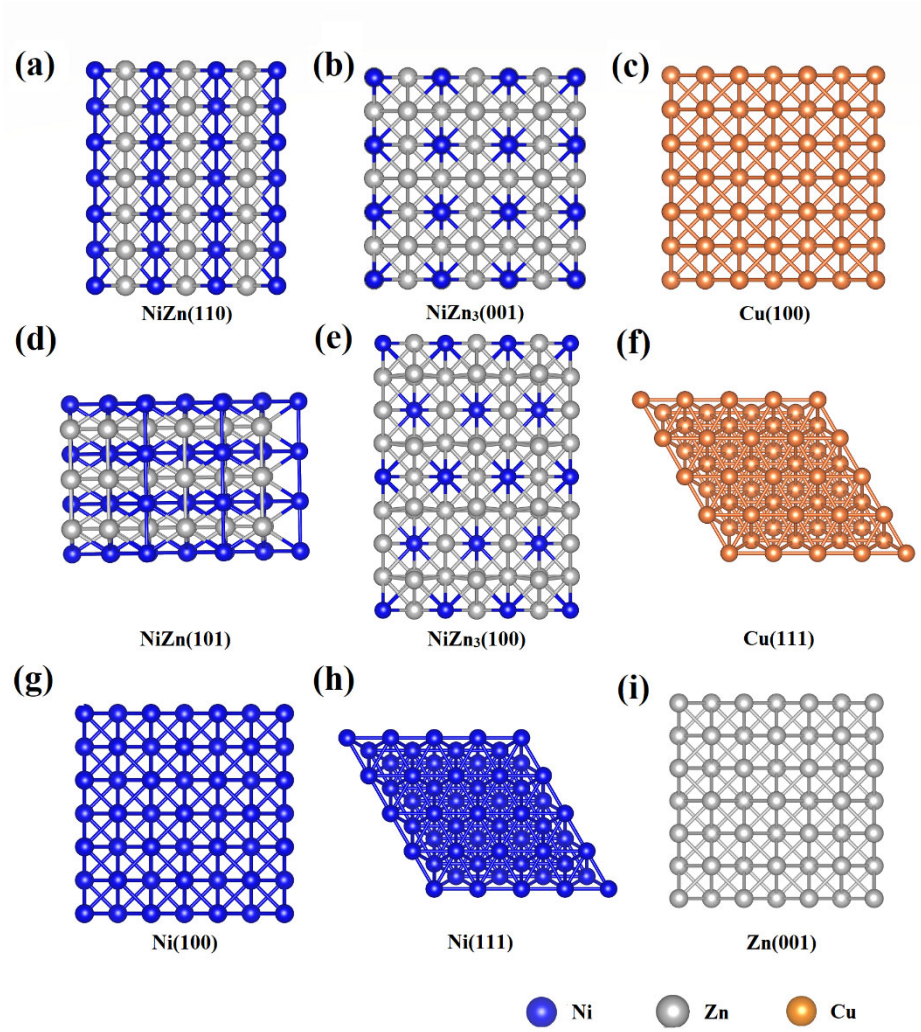

Fig. S1 Top view of **(a)** NiZn(110), **(b)** $NiZn_3$(001), **(c)** Cu(100), **(d)** NiZn(101), **(e)** $NiZn_3$(100), **(f)** Cu(111), **(g)** Ni(100), **(h)** Ni(111) and **(i)** Zn(001) crystal facets. Each crystal facet is composed of a 3 × 3 × 4 surface supercells model.

Table S1 Calculated lattice constants of the different facets.

Catalysts	Calculated lattice constant (Å)
NiZn(110)	a = 9.80, b = 11.59
NiZn(101)	a = 12.78, b = 8.20
$NiZn_3$(001)	a = b = 11.01
$NiZn_3$(100)	a = 11.01, b = 15.67
Cu(100)	a = b = 11.04
Cu(111)	a = 17.80, b = 10.27
Ni(100)	a = b = 10.53
Ni(111)	a = 17.20, b = 9.93
Zn(001)	a = b = 11.25

Table S2 Calculated adsorption energies of *CO_2, *CO and *H on the square geometric site. The trigonal sites were used as adsorption sites in Cu(111) and Ni(111).

Catalysts	ΔE_{CO2} (eV)	ΔE_{CO} (eV)	ΔE_{H} (eV)
NiZn(110)	−0.023	−1.28	−0.39
NiZn(101)	−0.026	−1.65	−0.51
$NiZn_3$(001)	−0.020	−0.92	−0.08
$NiZn_3$(100)	−0.017	−1.44	−0.45
Cu(100)	−0.023	−0.86	−0.11
Cu(111)	−0.019	−0.78	−0.14
Ni(100)	−0.030	−2.11	−0.52
Ni(111)	−0.024	−2.13	−0.61
Zn(001)	−0.015	−0.09	1.14

Table S3 Calculated free energy barriers of reaction steps from CO_2 to *CO.

Reaction steps	Free energy barrier on NiZn(110) (eV)	Free energy barrier on $NiZn_3$(001) (eV)	Free energy barrier on Cu(100) (eV)
CO_2 → *CO_2	−0.02	−0.01	−0.02
*CO_2 → *COOH	**0.09**	**0.21**	**0.53**
*COOH → *CO	−0.55	−0.45	−0.60

Table S4 Calculated free energy barriers of reaction steps from CO_2 to *HCOOH.

Reaction steps	Free energy barrier on NiZn(110) (eV)	Free energy barrier on $NiZn_3$(001) (eV)	Free energy barrier on Cu(100) (eV)
CO_2 → *CO_2	−0.02	−0.01	−0.02
*CO_2 → *OCHO	−0.46	−0.18	−0.16
*OCHO →*HCOOH	**0.62**	**0.53**	**0.45**

Table S5 Calculated free energy barriers of reaction steps along the pathway from CO to *CHO, *COH and *CO−CO.

Reaction steps	Free energy barrier on NiZn(110) (eV)	Free energy barrier on $NiZn_3$(001) (eV)	Free energy barrier on Cu(100) (eV)
CO → *CO	−1.21	−0.97	−0.82
*CO → *CHO	**0.57**	**0.60**	**0.70**
*CO → *COH	1.66	0.98	0.91
*CO →*CO−CO	1.57	1.24	0.91

Table S6 Calculated free energy barriers of C−C coupling reaction steps via *CHO intermediate.

Reaction steps	Free energy barrier on NiZn(110) (eV)	Free energy barrier on $NiZn_3$(001) (eV)	Free energy barrier on Cu(100) (eV)
*CO → *CHO	0.57	**0.60**	**0.70**
*CHO → *CHO−CO	**0.82**	0.45	0.15

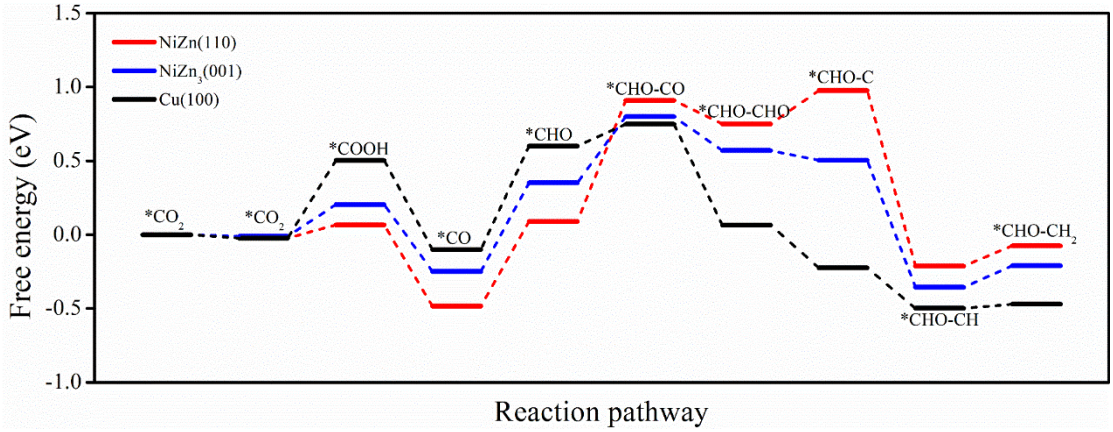

Fig. S2 Free energy profile from CO_2 to CHO−CH_2 via CHO−CHO intermediate on NiZn(110), $NiZn_3$(001) and Cu(100). *CHO−CO as the intermediate for C−C coupling.

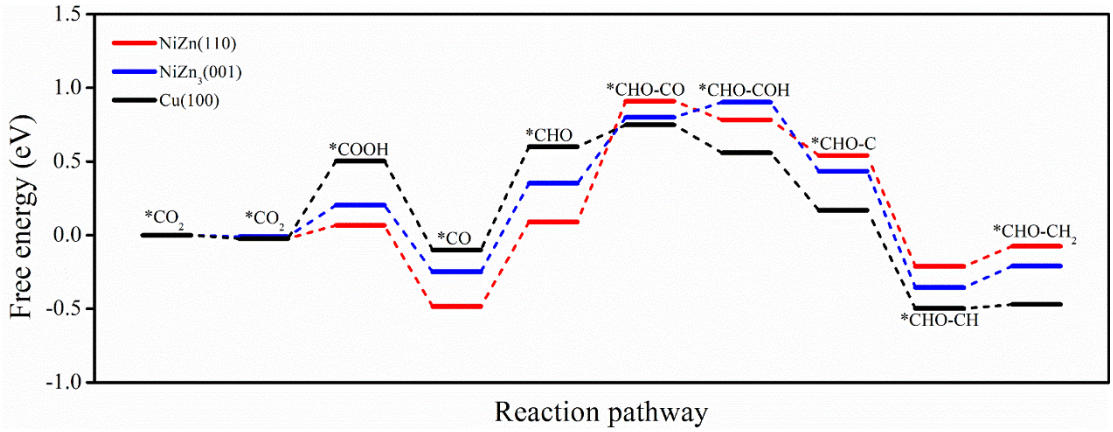

Fig. S3 Free energy profile from CO_2 to CHO−CH_2 via CHO−COH intermediate on NiZn(110), $NiZn_3$(001) and Cu(100). *CHO−CO as the intermediate for C−C coupling.

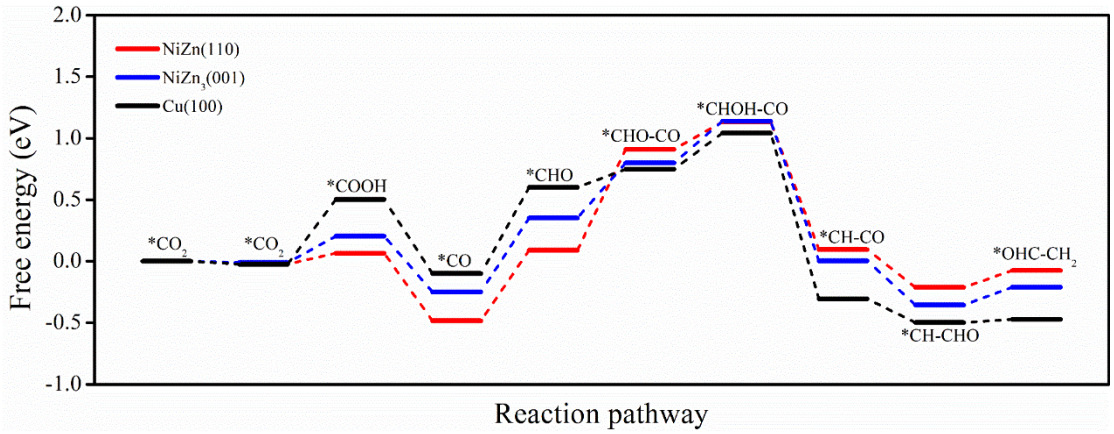

Fig. S4 Free energy profile from CO_2 to CHO−CH_2 via CHOH−CO intermediate on NiZn(110), $NiZn_3$(001) and Cu(100). *CHO−CO as the intermediate for C−C coupling.

Table S7 Calculated free energy barriers of C_2 products formation from CO_2 to *CHO−CH_2 via *CHO−CHO, *CHO−CO as the intermediate for C−C coupling.

Reaction steps	Free energy barrier on NiZn(110) (eV)	Free energy barrier on $NiZn_3$(001) (eV)	Free energy barrier on Cu(100) (eV)
*CO_2 → *CO_2	−0.02	−0.01	−0.02
*CO_2→*COOH	0.09	0.21	0.53
*COOH → *CO	−0.55	−0.45	−0.60
*CO →*CHO	0.57	**0.60**	**0.70**
*CHO → *CHO−CO	**0.82**	0.45	0.15
*CHO−CO → *CHO−CHO	−0.16	−0.23	−0.68
*CHO−CHO → *CHO−CHOH	0.23	−0.07	−0.29
*CHO−CHOH → *CHO−CH	−1.18	−0.86	−0.27
*CHO−CH→ *CHO−CH_2	0.14	0.15	0.03

Table S8 Calculated free energy barriers of C_2 products formation from CO_2 to *CHO−CH_2 via *CHO−COH, *CHO−CO as the intermediate for C−C coupling.

Reaction steps	Free energy barrier on NiZn(110) (eV)	Free energy barrier on $NiZn_3$(001) (eV)	Free energy barrier on Cu(100) (eV)
*CO_2 → *CO_2	−0.02	−0.01	−0.02
*CO_2→*COOH	0.09	0.21	0.53
*COOH → *CO	−0.55	−0.45	−0.60
*CO →*CHO	0.57	**0.60**	**0.70**
*CHO →*CHO−CO	**0.82**	0.45	0.15
*CHO−CO → *CHO−COH	−0.13	0.10	0.19
*CHO−COH → *CHO−C	−0.24	−0.47	−0.39
*CHO−C → *CHO−CH	−0.75	−0.79	−0.67
*CHO−CH→ *CHO−CH_2	0.14	0.15	0.03

Table S9 Calculated free energy barriers of C_2 products formation from CO_2 to *CHO−CH_2 via *CHO−COH, *CHO−CO as the intermediate for C−C coupling.

Reaction steps	Free energy barrier on NiZn(110) (eV)	Free energy barrier on $NiZn_3$(001) (eV)	Free energy barrier on Cu(100) (eV)
*CO_2 → *CO_2	−0.02	−0.01	−0.02
*CO_2→*COOH	0.09	0.21	0.53
*COOH → *CO	−0.55	−0.45	−0.60
*CO →*CHO	0.57	**0.60**	**0.70**
*CHO → *CHO−CO	**0.82**	0.45	0.15
*CHO−CO → *CHOH−CO	0.22	0.34	0.15
*CHOH−CO →*CH−CO	−1.04	−1.14	−1.35
*CHO−CHOH → *CHO−CH	−0.31	−0.36	−0.19
*CHO−CH → *CHO−CH_2	0.14	0.15	0.03

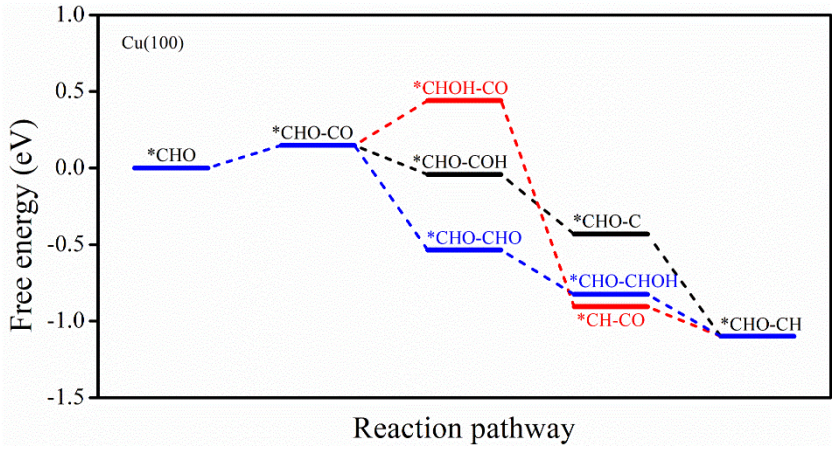

Fig. S5 Three pathways of *CHO−CO hydrogenation to *CHO−CH on Cu(100).

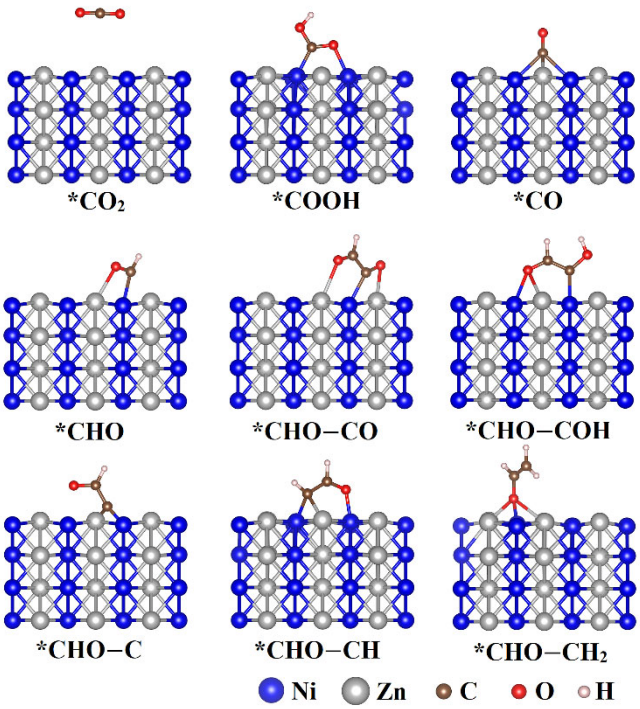

Fig. S6 Side view of intermediate species along the pathways from CO_2 to *CHO−CH_2 via *CHO−COH intermediate on NiZn(110).

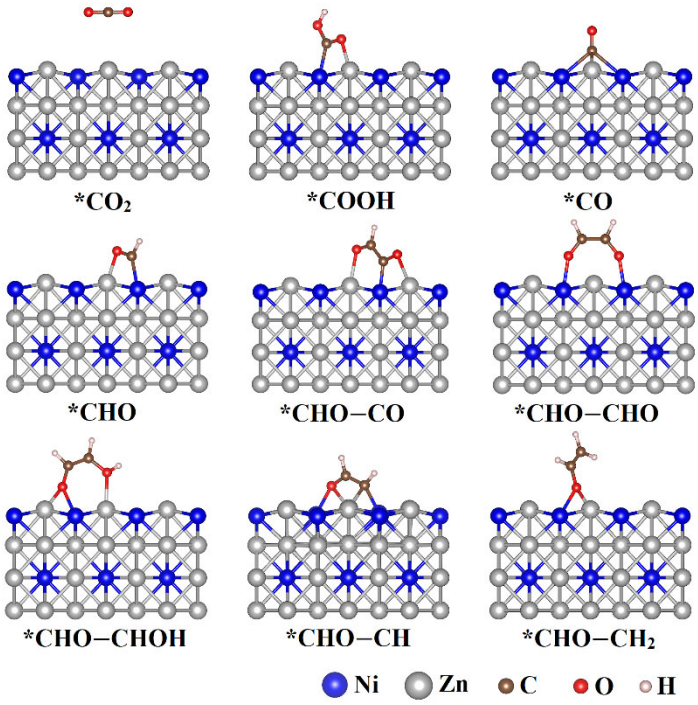

Fig. S7 Side view of intermediate species along the pathways from CO_2 to *CHO−CH_2 via *CHO−CHO intermediate on $NiZn_3$(001).

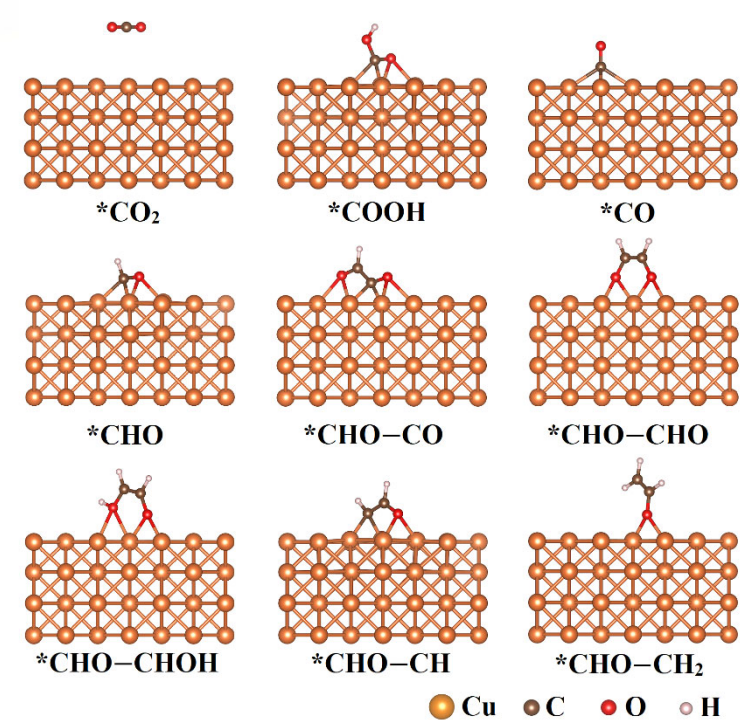

Fig. S8 Side view of intermediate species along the pathways from CO_2 to *CHO−CH_2 via *CHO−CHO intermediate on Cu(100).