Metal Substrate Engineering to Modulate CO_2 Hydrogenation to Methanol on Inverse Zr_3O_6/CuPd Catalysts

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Table S1 The details of setup for construction of Z/CuPd models.

parameters / catalysts	Supercell	Atom Layers	Fixed Layers	Vacuum Gap
Z /CuPd(100)-Cu	5×5	4	bottom 2	12Å
Z /CuPd(100)-Pd	5×5	4	bottom 2	12Å
Z /CuPd(110)	5×4	4	bottom 2	11Å
Z /CuPd(111)-Cu	4×4	8	bottom 4	12Å
Z /CuPd(111)-Pd	4×4	8	bottom 4	12Å

Table S2 Bader charge analysis(in |e|) of CO_2 adsorbed on Zr_3O_6/CuPd catalysts.

	Z/CuPd(100) -Cu	Z/CuPd(100) - Pd	Z/CuPd(110)	Z/CuPd(111) - Cu	Z/CuPd(110) - Pd
O_1(Zr)	-1.10	-1.12	-1.12	-1.11	-1.11
O_2(CuPd)	-1.04	-1.00	-1.07	-1.04	-1.02
C	1.22	1.44	1.45	1.45	1.56
total	-0.92	-0.68	-0.74	-0.70	-0.57

Table S3 Adsorption energies of key intermediates involved in methanol synthesis progress over Zr_3O_6/CuPd catalysts.

species / catalysts	Z/CuPd(100)-Cu	Z/CuPd(100)-Pd	Z/CuPd(110)	Z/CuPd(111)-Cu	Z/CuPd(111)-Pd
H	-2.86	-2.72	-2.90	-2.82	-2.85
O	-6.28	-5.45	-5.67	-6.32	-5.88
H_2	-0.31	-0.33	-0.44	-0.37	-0.50
CO_2	-1.51	-1.65	-1.67	-1.42	-1.73

CO	-1.23	-2.36	-2.61	-1.59	-2.23
OH	-5.47	-4.95	-5.39	-5.48	-5.28
HCOO	-4.65	-4.39	-4.66	-4.99	-4.81
COOH	-3.93	-4.00	-4.00	-4.20	-4.37
HCOOH	-1.62	-1.68	-2.02	-1.56	-1.73
CH_2OOH	-4.63	-4.26	-4.47	-4.73	-4.54
HCO	-3.60	-3.65	-4.04	-3.69	-4.01
CH_2O	-2.20	-2.20	-2.53	-2.37	-2.54
CH_3O	-4.75	-4.23	-4.70	-4.69	-4.50
CH_2OH	-3.29	-3.15	-3.25	-3.26	-3.48
CH_3OH	-1.56	-1.55	-1.87	-1.59	-1.56
H_2O	-1.29	-1.30	-1.63	-1.33	-1.46

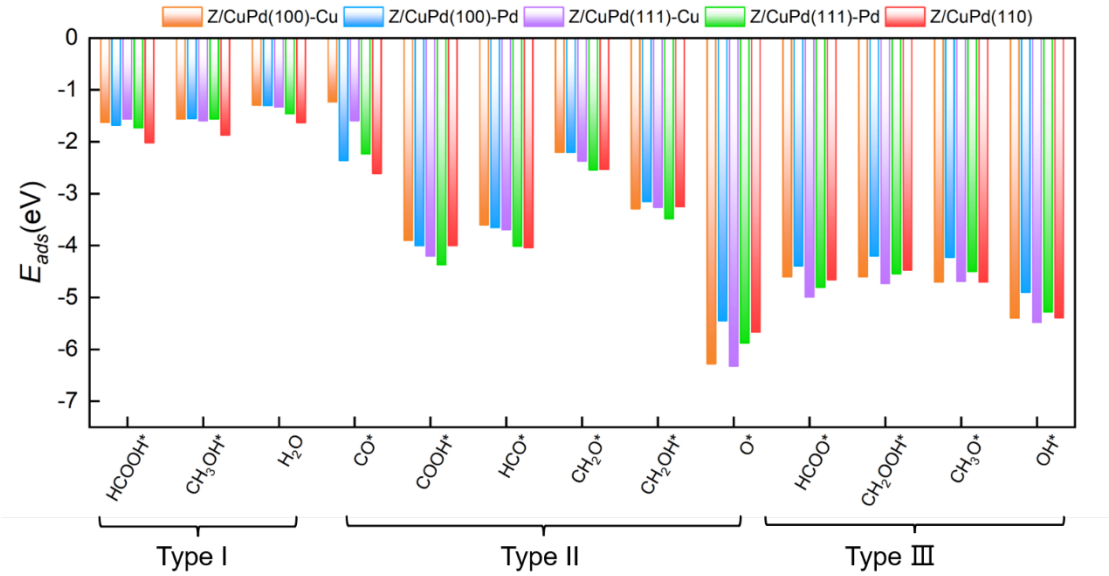


Figure S1 Histogram of adsorption energies of key intermediates in the methanol synthesis process.

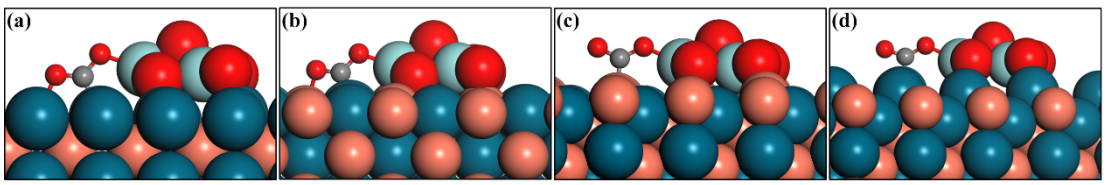


Figure S2 DFT optimized geometry configuration of CO_2 adsorbed on (a) Z/CuPd(100)-Pd (b) Z/CuPd(110) (c) Z/CuPd(111)-Cu (d) Z/CuPd(111)-Pd

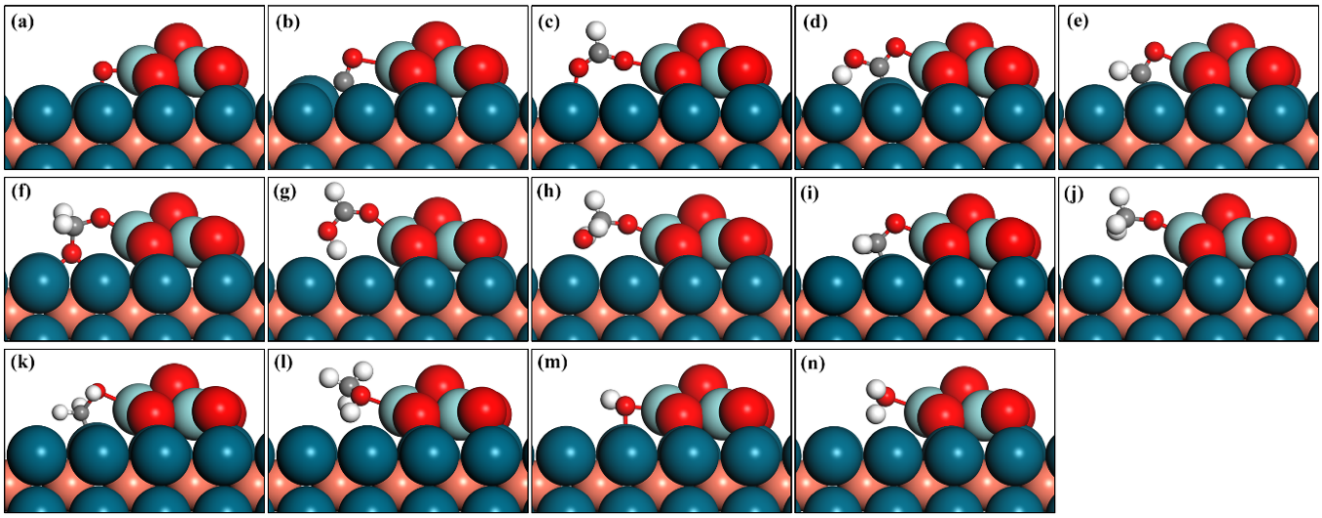


Figure S3 Side views of the optimized structures of key intermediates adsorbed on Z/PdCu(100)-Pd (a) O* (b) CO* (c) HCOO* (d) COOH* (e) HCO* (f) CH_2OO* (g) HCOOH* (h) CH_2OOH* (i) CH_2O* (j) CH_3O* (k) CH_2OH* (l) CH_3OH* (m) OH* (n)H_2O*

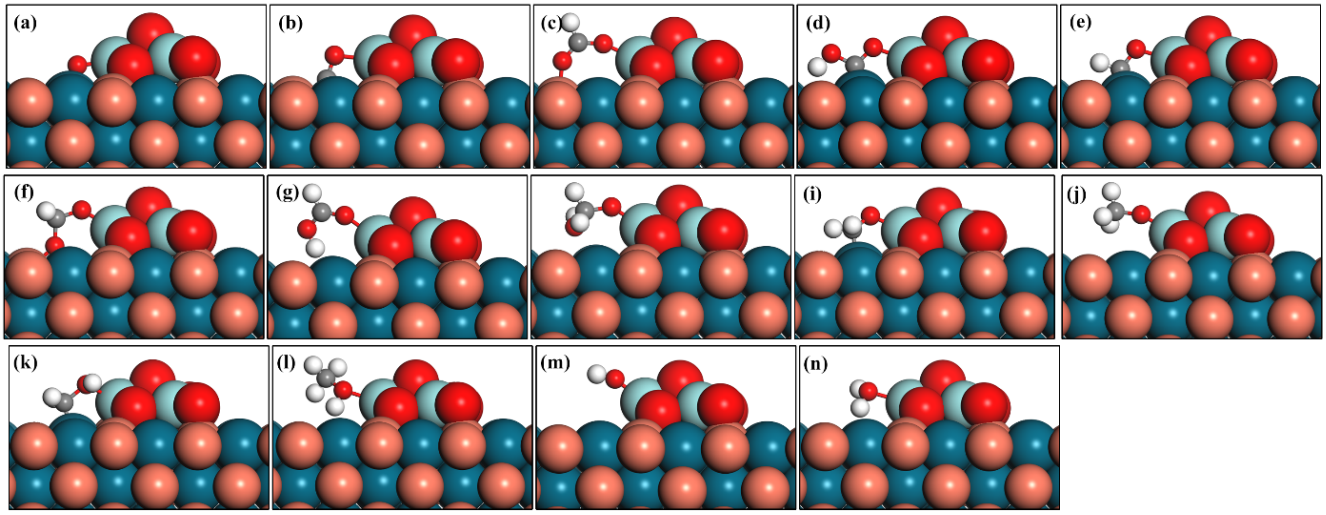


Figure S4 Side views of the optimized structures of key intermediates adsorbed on Z/PdCu(110) (a) O* (b) CO* (c) HCOO* (d) COOH* (e) HCO* (f) CH_2OO* (g) HCOOH* (h) CH_2OOH* (i)

CH_2O* (j) CH_3O* (k) CH_2OH* (l) CH_3OH* (m) OH* (n)H_2O*

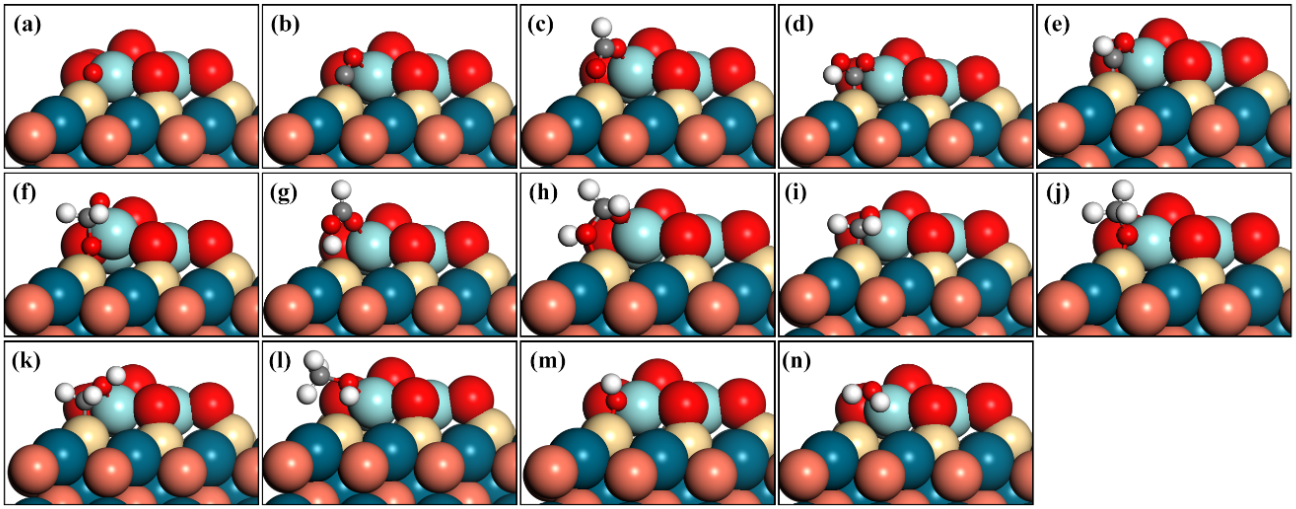


Figure S5 Side views of the optimized structures of key intermediates adsorbed on Z/PdCu(111)-Cu (a) O* (b) CO* (c) HCOO* (d) COOH* (e) HCO* (f) CH_2OO* (g) HCOOH* (h) CH_2OOH* (i) CH_2O* (j) CH_3O* (k) CH_2OH* (l) CH_3OH* (m) OH* (n)H_2O*

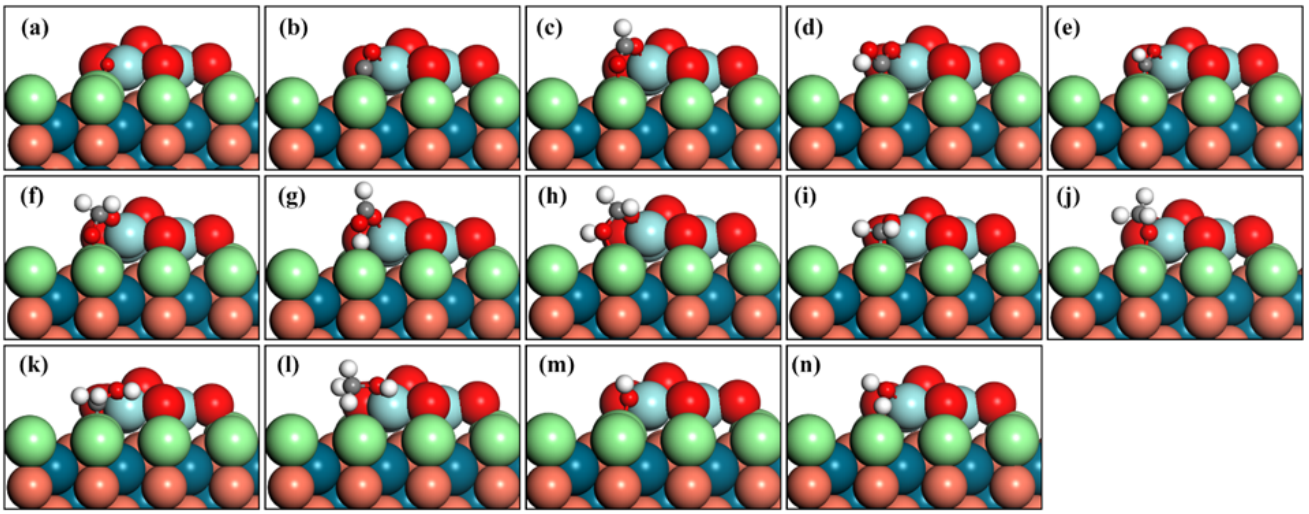


Figure S6 Side views of the optimized structures of key intermediates adsorbed on Z/PdCu(111)-Pd (a) O* (b) CO* (c) HCOO* (d) COOH* (e) HCO* (f) CH_2OO* (g) HCOOH* (h) CH_2OOH* (i) CH_2O* (j) CH_3O* (k) CH_2OH* (l) CH_3OH* (m) OH* (n)H_2O*

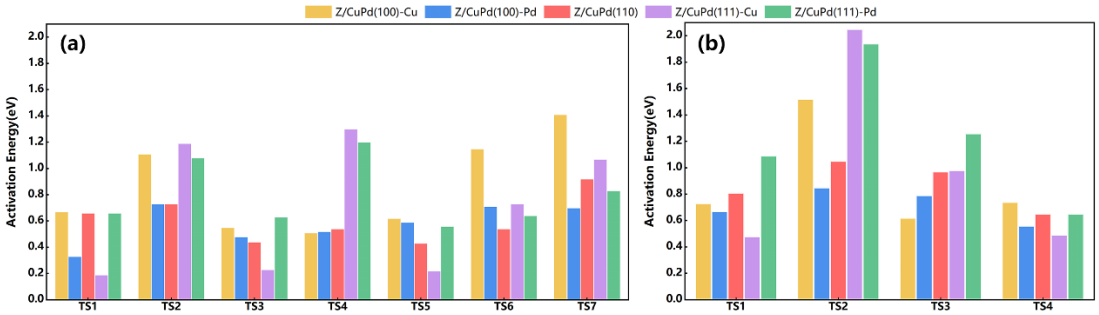
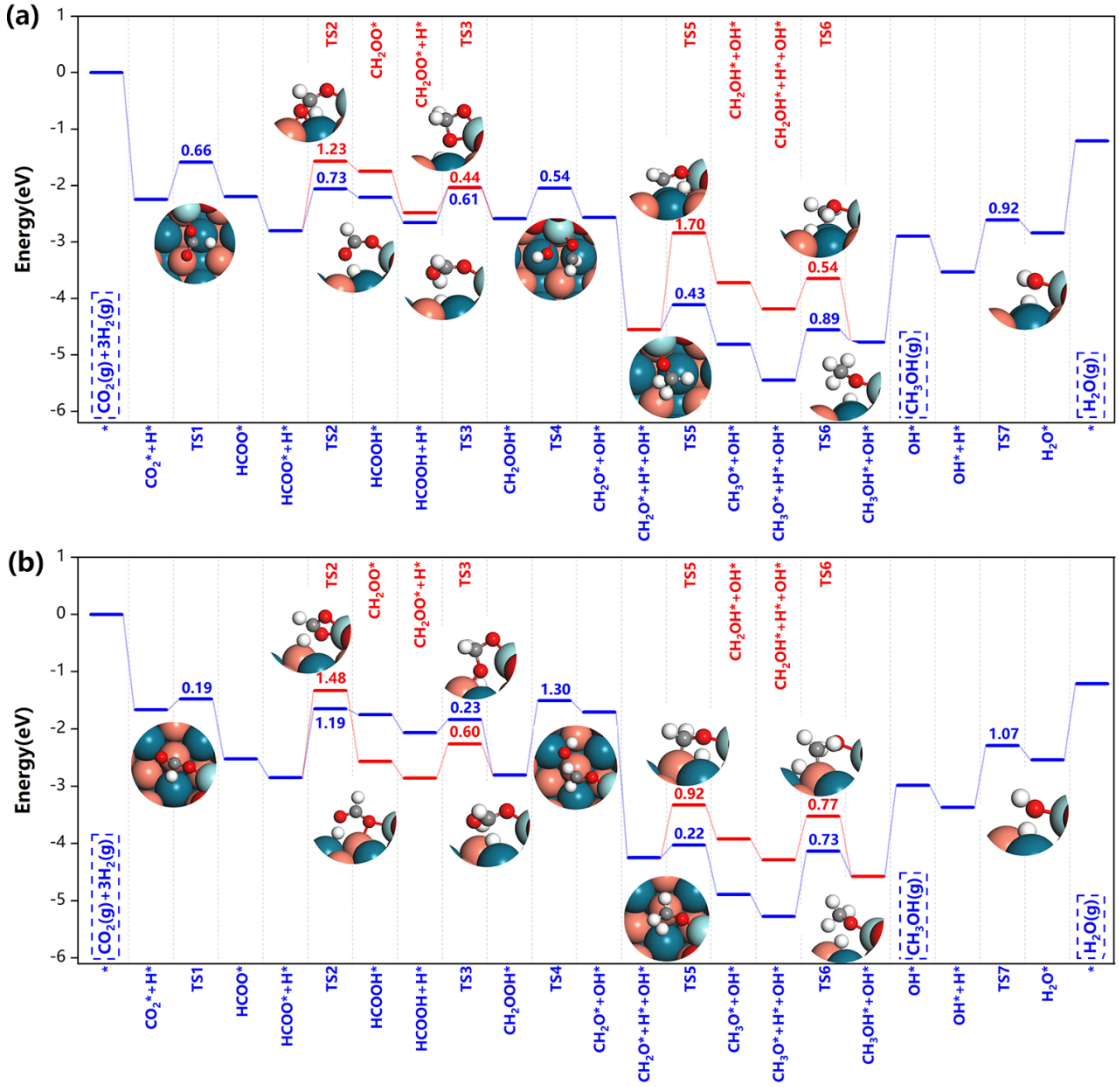


Figure S7 The lowest energy barrier along (a) Formate pathway (b) RWGS+CO-hydro pathway.



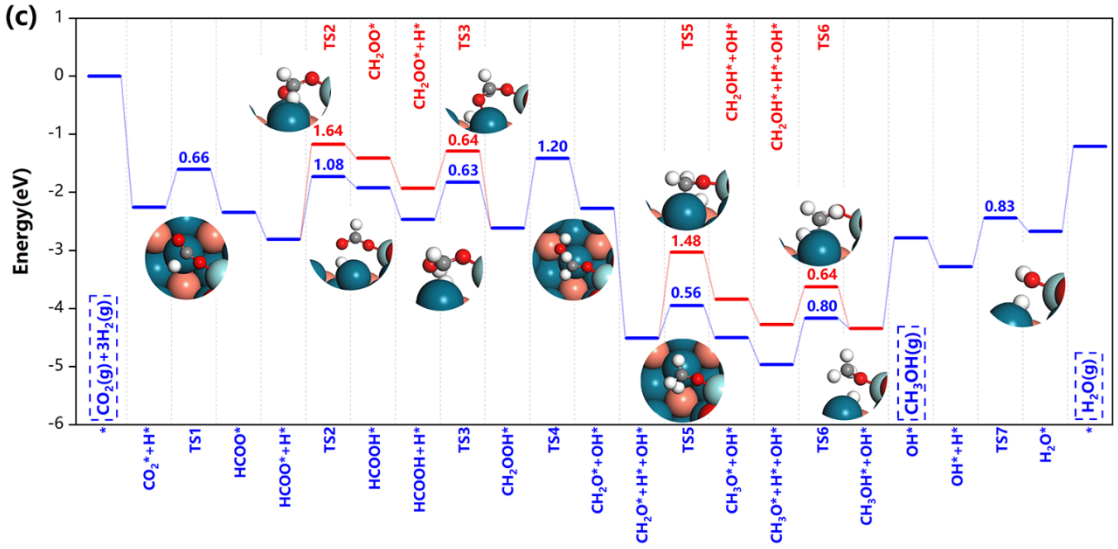
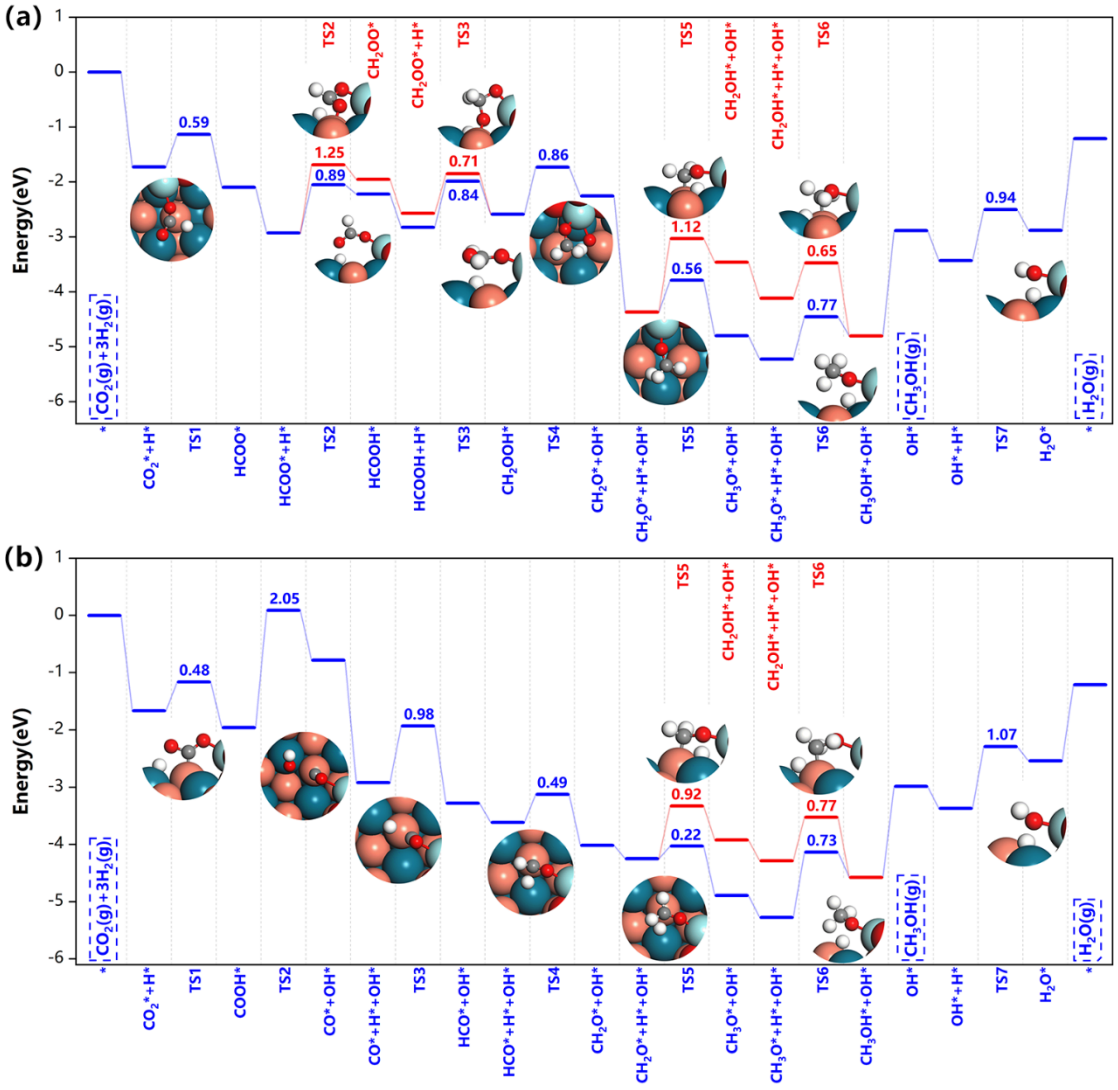


Figure S8 Potential energy diagrams and corresponding transition state structures of methanol formation over (a) Z/CuPd(110) (b) Z/CuPd(111)-Cu (c) Z/CuPd(111)-Pd along formate pathway.



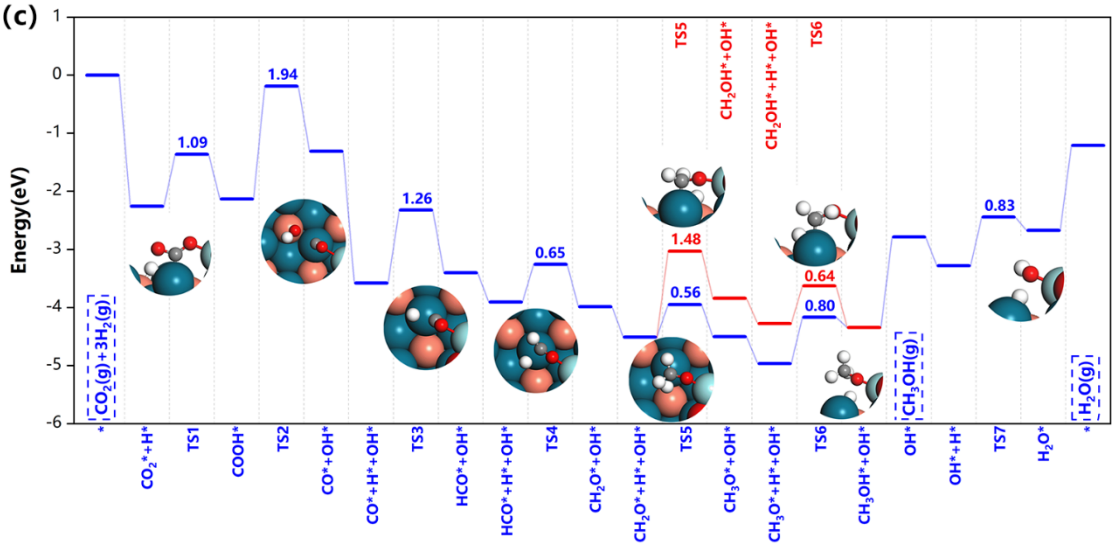


Figure S9 Potential energy diagrams and corresponding transition state structures of methanol formation over (a) Z/CuPd(110) (b) Z/CuPd(111)-Cu (c) Z/CuPd(111)-Pd along RWGS + CO-hydro pathway.

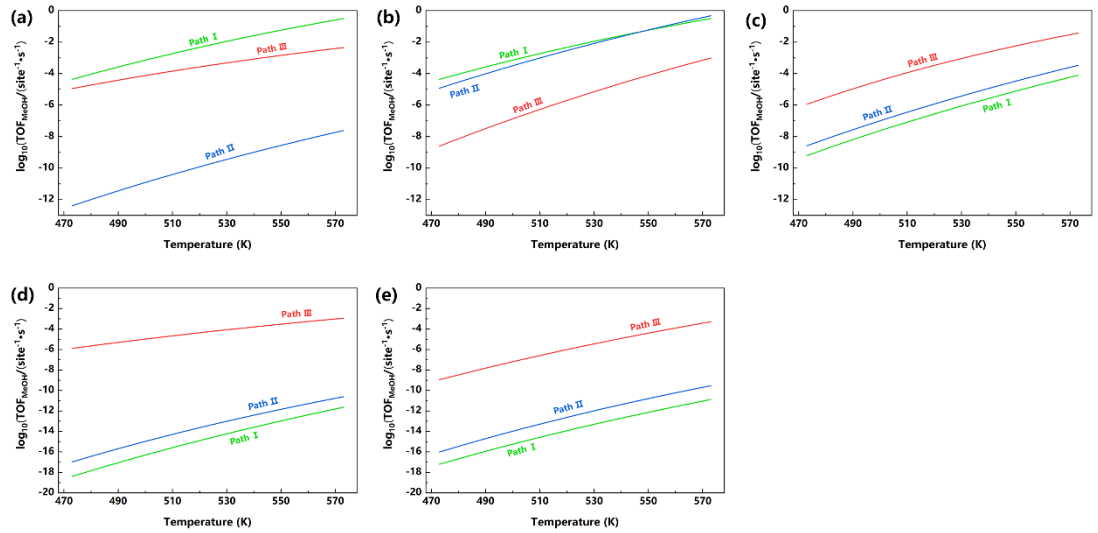


Figure S10 The calculated logarithm turnover frequency (TOF) of MeOH formation pathways over (a) Z/CuPd(100)-Cu (b) Z/CuPd(100)-Pd (c) Z/CuPd(110) (d) Z/CuPd(111)-Cu and (e) Z/CuPd(111)-Pd at reactant pressure of 5 bar.

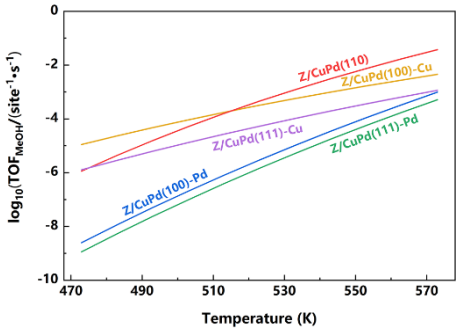


Figure S11 The logarithm turnover frequency (TOF) of CO_2 direct activation pathway over Zr_3O_6/CuPd catalysts.