Supporting Information

Mechanistic Insight into C-C Coupling over Fe-Cu Bimetallic Catalysts in CO_2 Hydrogenation

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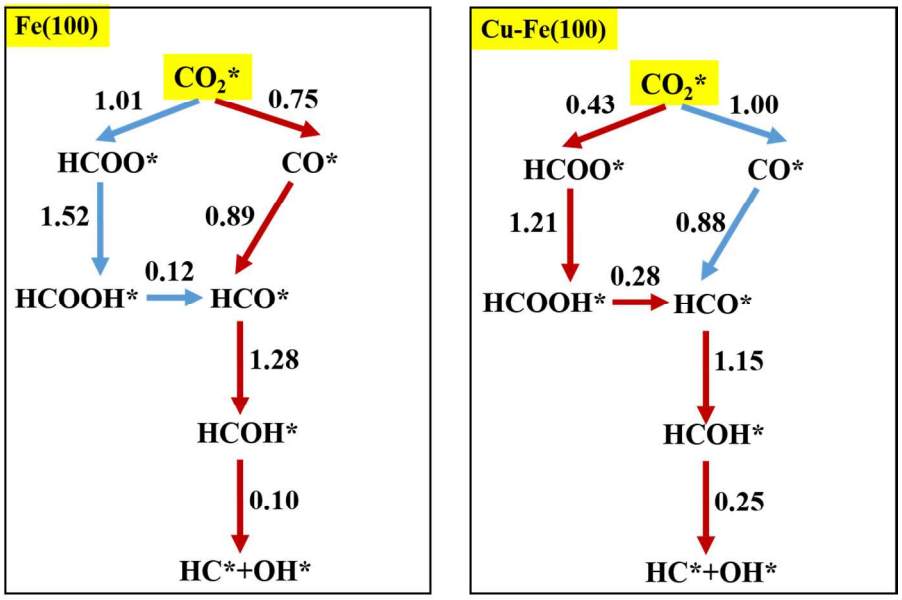
Table S1. Activation barriers without and with ZPE corrections (E_a and E_a^{ZPE}) for elementary steps examined for CH_4 and C_2H_4 production in CO_2 conversion on Fe(100) and Cu-Fe(100).

Elementary Steps	Fe(100)		Cu-Fe(100)	
	E_{act} (eV)	E_{act}^{ZPE} (eV)	E_{act} (eV)	E_{act}^{ZPE} (eV)
CO_2*+H* → HCOO*	1.00	1.01	0.39	0.43
CO_2* → CO*+O*	0.80	0.75	1.06	1.00
CO* → HCO*	0.89	0.89	0.87	0.88
HCOO*+H* → HCOOH*	1.59	1.52	1.27	1.21
HCOOH* → HCO*+OH*	0.18	0.12	0.35	0.28
HCO*+H* → HCOH*	1.32	1.28	1.22	1.15
HCOH* → HC*+OH*	0.13	0.10	0.32	0.25
CH*+CH* → CH-CH*	1.23	1.25	0.76	0.77
CH-CH*+H* → CH-CH_2*	0.58	0.56	0.67	0.64
CH-CH_2*+H* → CH_2-CH_2*	0.59	0.65	0.76	0.82
CH*+H* → CH_2*	0.76	0.80	0.73	0.75
CH_2*+H* → CH_3*	0.93	0.98	1.01	1.06
CH_3*+H* → CH_4*	0.82	0.79	0.64	0.62

Table S2. The imaginary vibrational frequency corresponding to each transition state involved in CO_2 conversion on Fe(100) and Cu-Fe(100).

Elementary Steps	Fe(100)	Cu-Fe(100)
	Imaginary vibrational frequency for TS (cm^{-1})	Imaginary vibrational frequency for TS (cm^{-1})
CO_2*+H* → COOH*	-1249.072814	-1337.603097
CO_2*+H* → HCOO*	-766.901346	-430.811624
CO_2* → CO*+O*	-380.061631	-229.392080
CO*+H* → HCO*	-679.205702	-560.379101
CO*+H* → COH*	-1168.417463	-1377.61389
HCOO*+H* → HCOOH*	-1157.876458	-1156.276262
HCOOH* → HCO*+OH*	-336.53809	-227.696228
HCO*+H* → HCOH*	-1143.12878	-1203.806235
HCOH* → HC*+OH*	-360.196962	-354.411281
C*+H* → CH*	-817.021944	-854.226665
CH*+H* → CH_2*	-786.297013	-842.989575
CH_2*+H* → CH_3*	-826.293726	-751.838013
CH_3*+H* → CH_4*	-1032.396269	-1012.541631
C*+C* → C-C*	-287.365716	-228.628722
C*+CH* → C-CH*	-380.375873	-364.437477
C*+CH_2* → C-CH_2*	-399.760619	-339.91668
C*+CH_3* → C-CH_3*	-464.238467	-436.023667
CH*+CH* → CH-CH*	-419.114349	-402.417369
CH*+CH_2* → CH-CH_2*	-436.920945	-424.405125
CH*+CH_3* → CH-CH_3*	-508.734597	-395.725138
CH_2*+CH_2* → CH_2-CH_2*	-421.823244	-468.065295
CH_2*+CH_3* → CH_2-CH_3*	-451.892461	-447.439683
CH_3*+CH_3* → CH_3-CH_3*	-572.595699	-640.986997
CH-CH*+H* → CH-CH_2*	-857.788849	-864.137826
CH-CH_2*+H* → CH_2-CH_2*	-723.440646	-636.934136
CH_2-CH_2*+H* → CH_2-CH_3*	-903.906463	-1021.17515
CH_2-CH_3*+H* → CH_3-CH_3*	-1020.42547	-993.690613



(a) (b)

Figure S1. Reaction pathways for CH* formation from CO_2 hydrogenation on (a) Fe(100) and (b) the Cu-Fe(100) surface at 4/9 ML Cu coverage. ZPE corrected barriers are given in eV. (The networks connected with red arrows represent the preferred path for CO_2 conversion to CH*.)

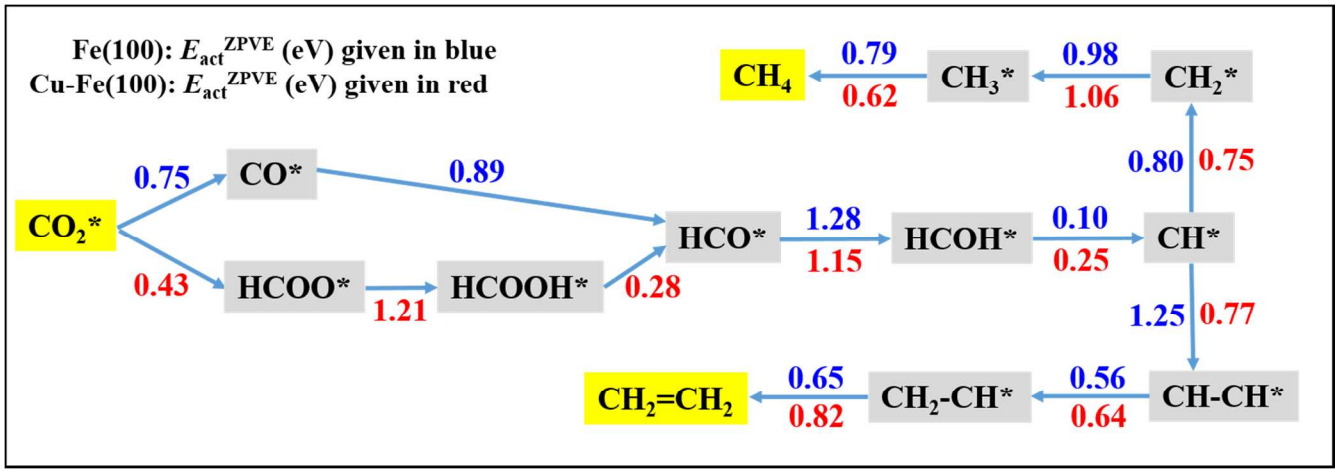


Figure S2. Reaction pathways for production of CH_4 and C_2H_4 from CO_2 on Fe(100) and the Cu-Fe(100) surface at 4/9 ML coverage. ZPE corrected barriers are given in eV.