Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Hetero-Bimetallic Paddlewheel Complexes for Enhanced CO_2 Reduction Selectivity: A First Principles Study

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SUPPLEMENTARY INFORMATION

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Table S1: Adsorption free energies of reaction products on the paddlewheel complexes. Negative values indicate favorable binding. Values given in eV.

	Site	H_2	CO_2	HCOOH	CO	CH_2O	CH_3OH	CH_4	H_2O
Cu-Cu	Cu	0.27	0.40	0.20	0.31	0.15	0.12	0.33	0.14
Cu-Mn	Cu	0.31	0.45	0.33	-0.20	0.24	0.23	0.40	0.18
	Mn	0.07	0.07	-0.37	-0.23	-0.32	-0.42	0.08	-0.50
Cu-Co	Cu	0.21	0.42	0.12	0.14	0.09	0.01	0.29	-0.02
	Co	0.12	0.12	-0.00	-0.23	-0.07	-0.11	0.18	-0.13
Cu-Ni	Cu	0.27	0.43	0.23	0.11	0.16	0.11	0.36	0.09
	Ni	0.22	0.33	0.22	0.15	0.15	0.11	0.32	0.19

Table S2: Geometric parameters of the paddlewheel complexes. Intermetallic bond distances ($R_{Cu\text{-}X}$) given in Å and bond angles ($A_{O\text{-}X\text{-}O}$) given in degrees.

	$R_{Cu\text{-}X}$	$A_{O\text{-}Cu\text{-}O}$	$A_{O\text{-}X\text{-}O}$
Cu-Mn	2.812	175.5	152.9
Cu-Co	2.438	170.6	178.8
Cu-Ni	2.445	171.1	177.9
Cu-Cu	2.573	172.0	172.0

Table S3: Löwdin spin populations and relative electronic energies on the paddlewheel complexes. AF refers to an antiferromagnetically coupled spin state while FM refers to a ferromagnetic spin state. Column headings refer to the metal site with X being the substituent metal (Mn, Co, Ni, or Cu).

	Spin State	Cu	X	Relative Energy (kcal mol^{-1})
Cu-Cu	FM3	0.6180	0.6180	1.7
	AF1	0.6101	-0.6101	0.0
Cu-Mn	FM7	0.6534	4.6600	1.3
	AF5	-0.5301	4.6028	0.0
Cu-Co	FM5	0.6585	2.6129	3.6
	AF3	-0.5318	2.6066	3.3
	FM3	0.6717	0.9552	0.0
	AF1	0.5534	-0.9784	1.0
Cu-Ni	FM4	0.6683	1.6150	4.8
	FM2	0.6296	0.0061	0.0

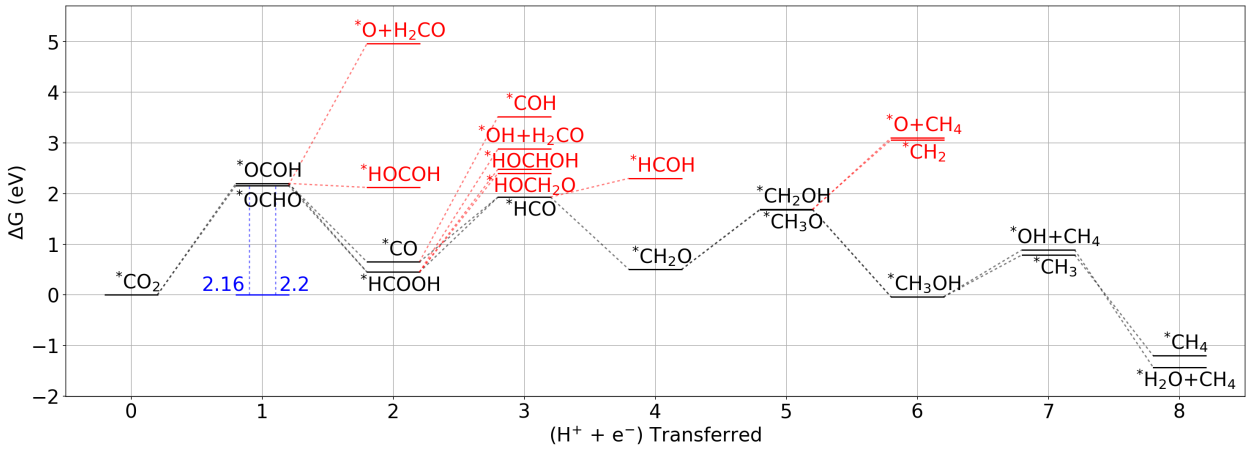

Figure S1: Free energy reaction mechanism for the reduction of CO_2 on the Cu site of the Cu-Zn paddlewheel complex. Competing intermediates shown in red. Limiting potential values shown in blue and given in eV.

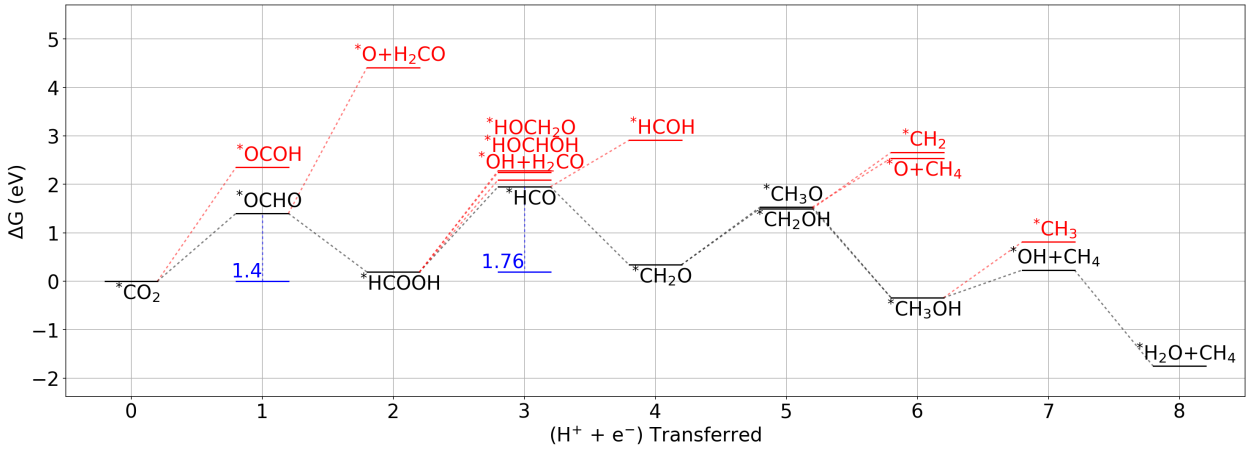

Figure S2: Free energy reaction mechanism for the reduction of CO_2 on the Zn site of the Cu-Zn paddlewheel complex. Competing intermediates shown in red. Limiting potential values shown in blue and given in eV.

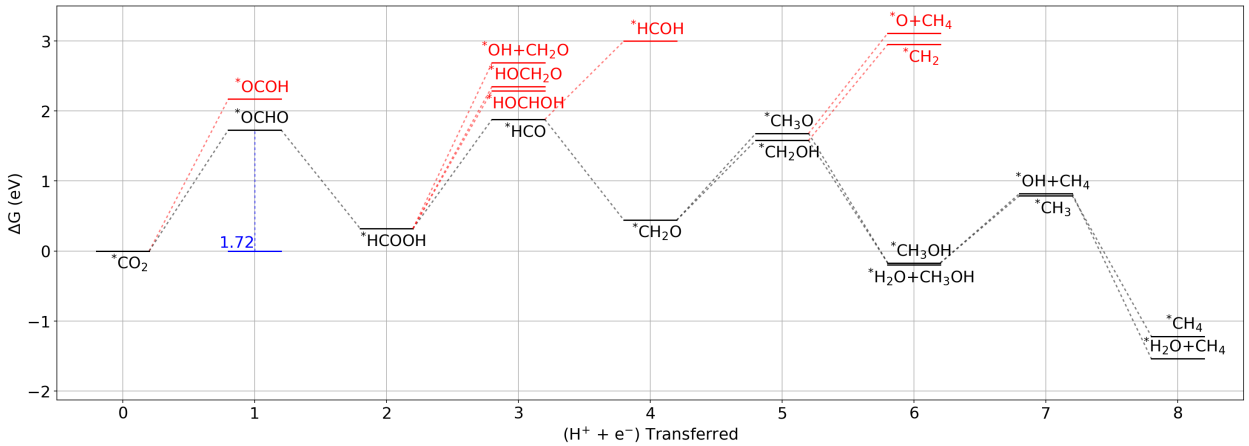

Figure S3: Free energy reaction mechanism for the reduction of CO_2 on the Cu site of the Cu-Co paddlewheel complex. Competing intermediates shown in red. Limiting potential values shown in blue and given in eV.