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Supplementary Materials

Theoretical Insights into Electrocatalytic CO_2 Reduction to C_2H_4 via Bridging-Mode Asymmetric Coupling over Bimetallic Triatomic Clusters

Shilin Wei, Hongguang Wang, Peiyao Bai and Lang Xu *

Jiangsu Key Laboratory for Clean Utilization of Carbon Resources, School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221116, China
* Correspondence: lang.xu@cumt.edu.cn

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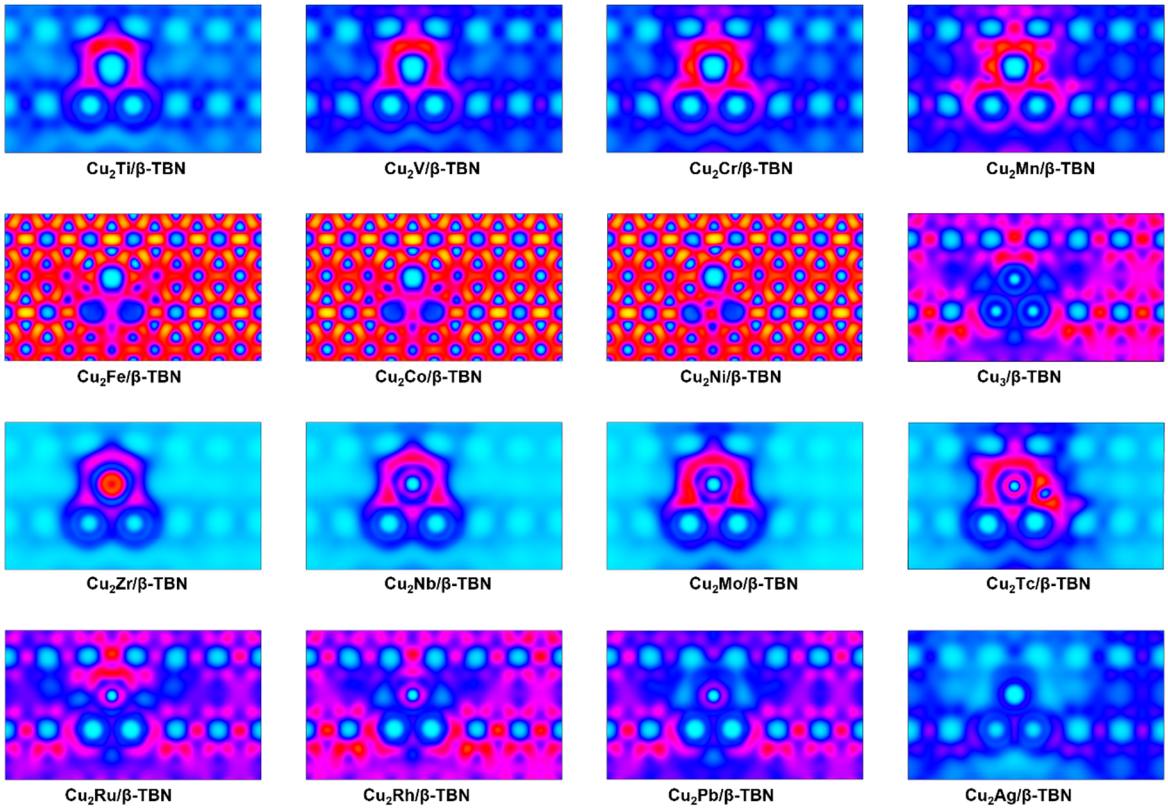


Figure S1. Electron localization function (ELF) maps for representative Cu_2TM/β-TBN systems. Blue corresponds to regions of low electron localization and red to regions of high electron localization.

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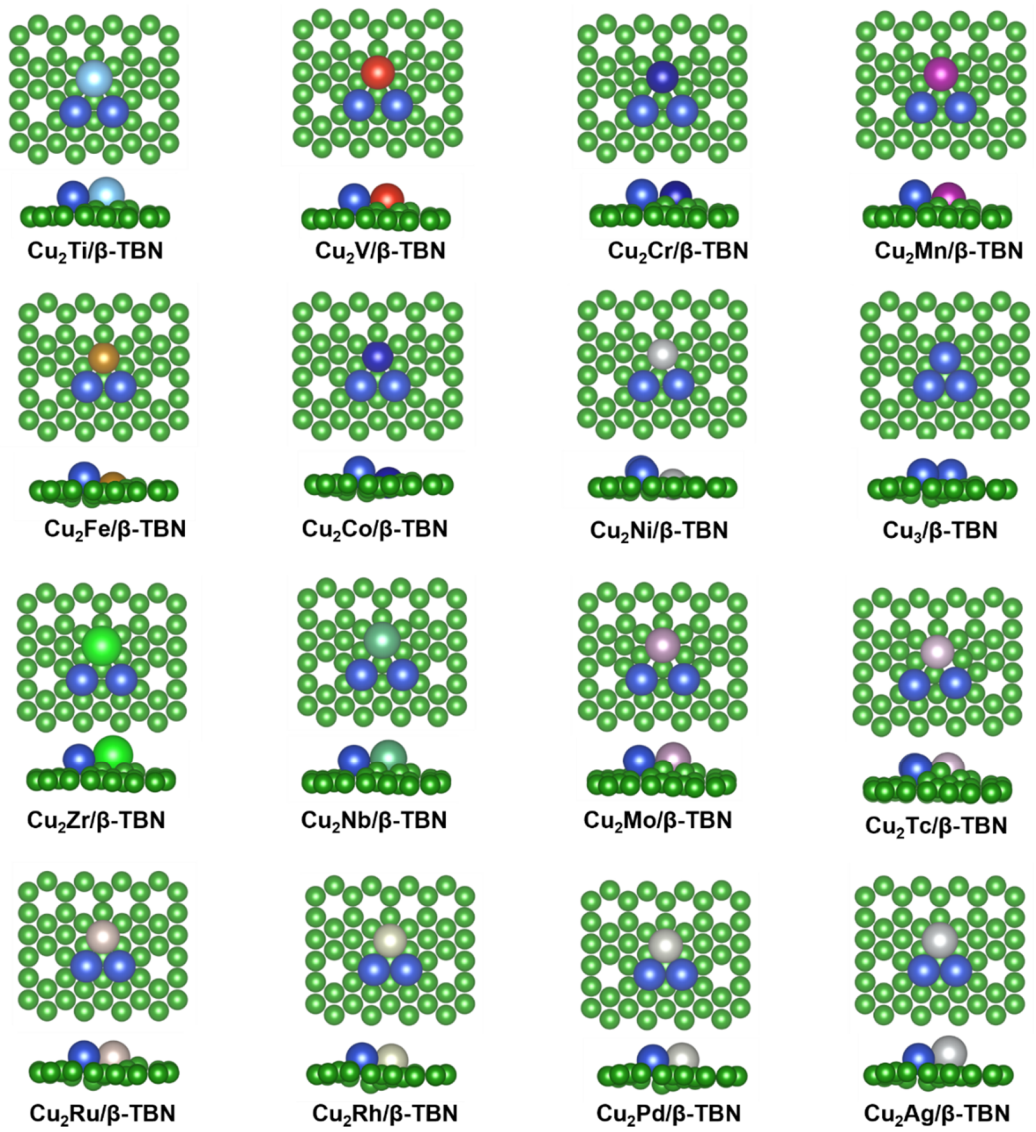


Figure S2. Schematic illustration of Cu_2TM/β-TBN with different TM dopants.

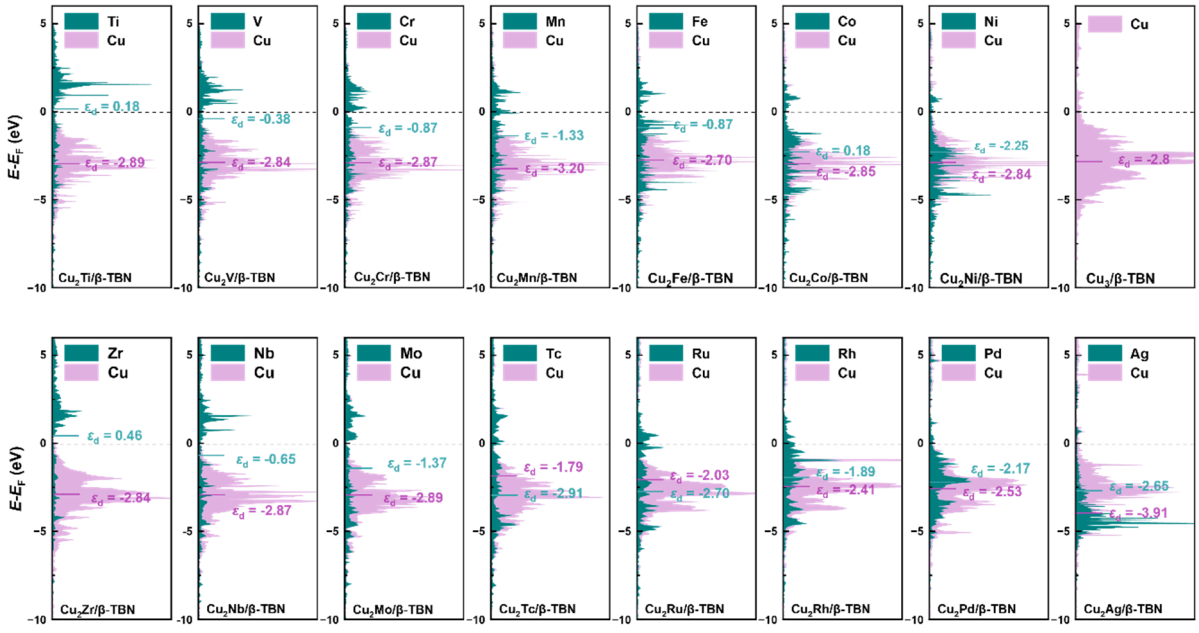


Figure S3. Density of states plots of Cu_2TM/β-TBN.

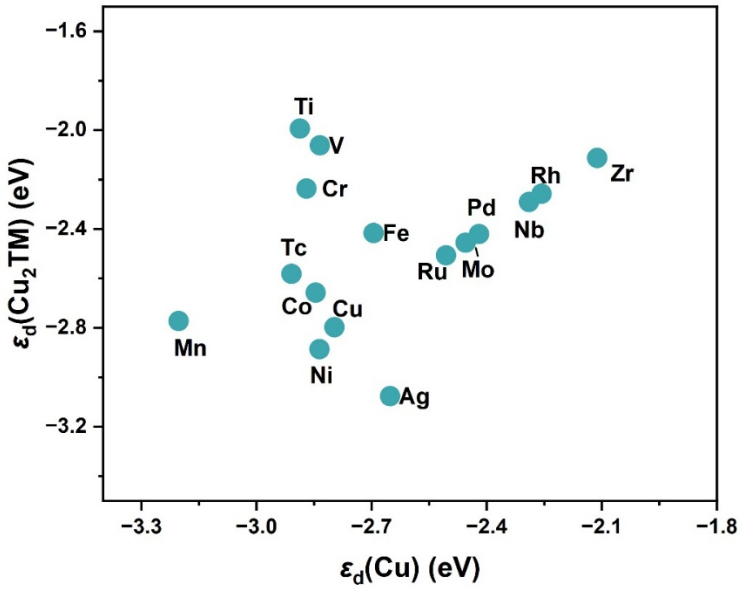


Figure S4. Correlation between ε_d(Cu) and ε_d(Cu_2TM) in the Cu_2TM/β-TBN structures.

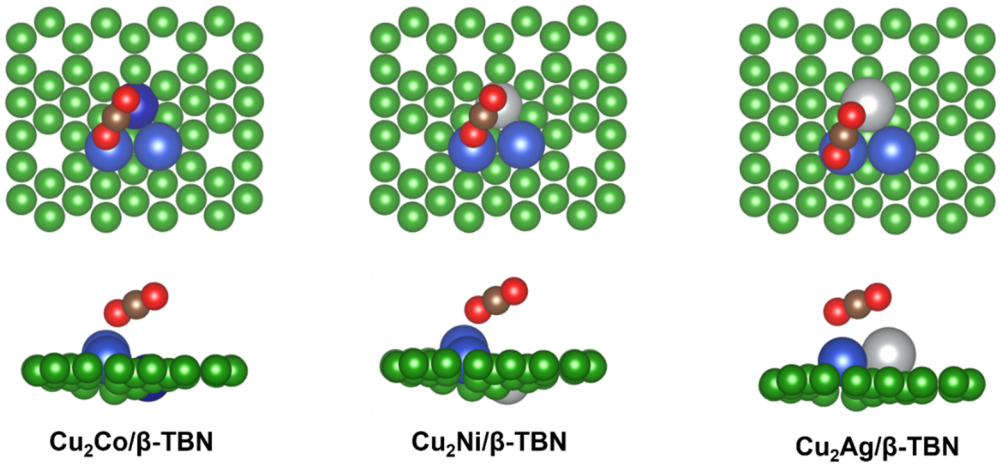


Figure S5. Structural illustrations of CO_2 adsorbed on Cu_2Co/β-TBN, Cu_2Ni/β-TBN, and Cu_2Ag/β-TBN.

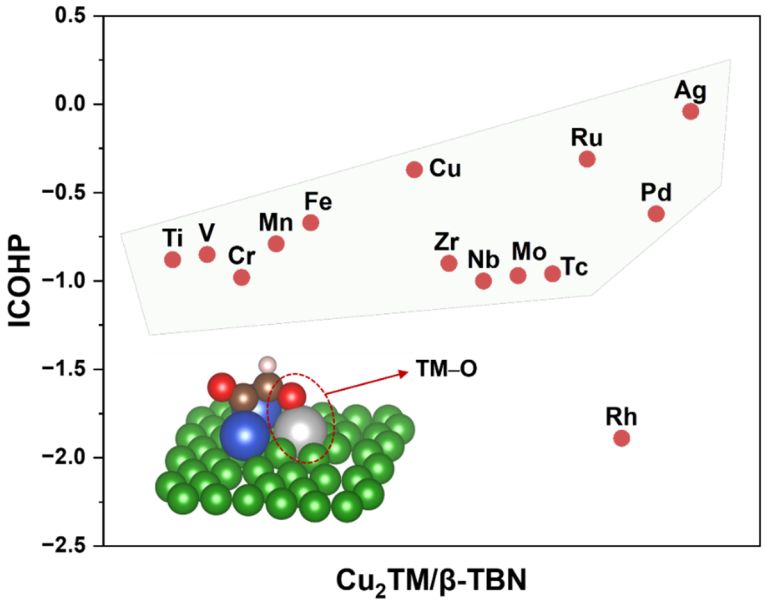


Figure S6. Distribution of ICOHP values for the TM–O bonds in *CHO+*CO adsorbed on Cu_2TM/β-TBN (TM = Ti, V, Cr, Mn, Fe, Cu, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag).

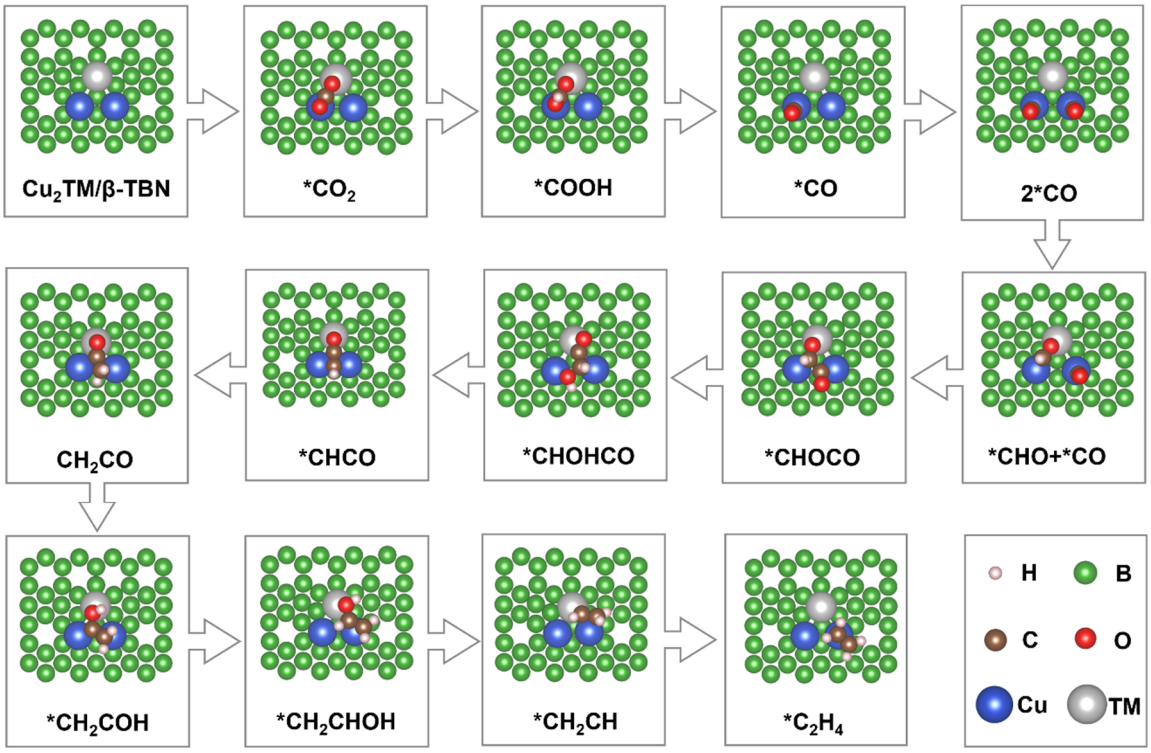


Figure S7. Proposed reaction pathways for the conversion of CO_2 to C_2H_4 via electrocatalytic reduction on Cu_2TM/β-TBN.

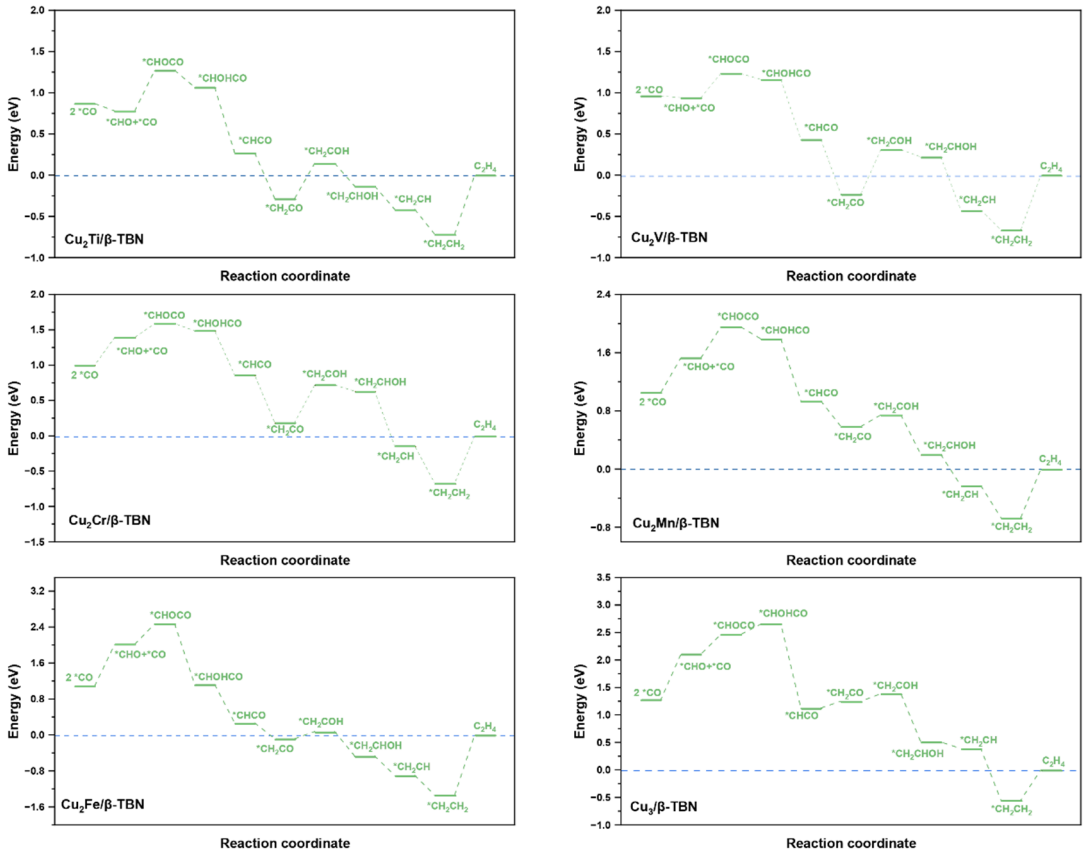


Figure S8. Free energy diagrams for the electrocatalytic reduction of 2*CO to C_2H_4 on Cu_2TM/β-TBN (TM = Ti, V, Cr, Mn, Fe, Cu).

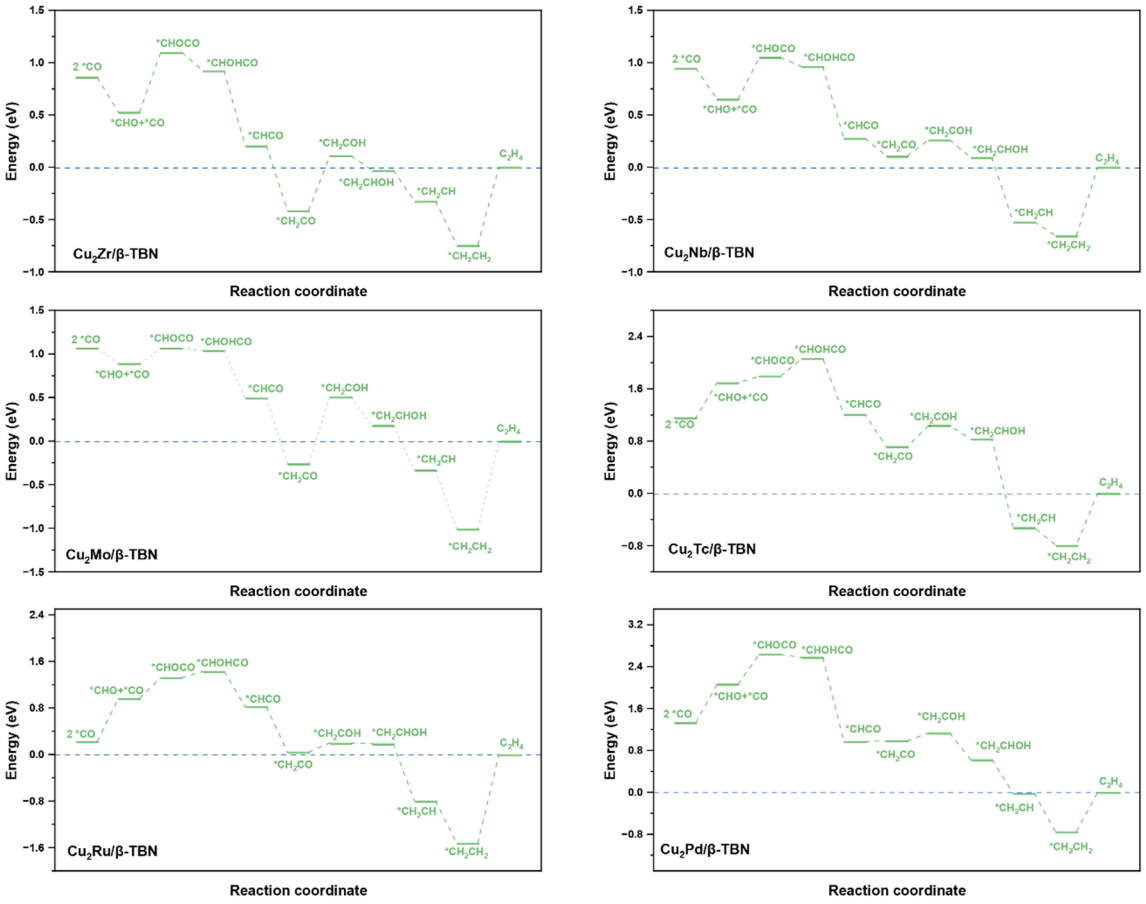


Figure S9. Free energy diagrams for the electrocatalytic reduction of 2*CO to C_2H_4 on Cu_2TM/β-TBN (TM = Zr, Nb, Mo, Tc, Ru, Pd).

Table S1. Summary of interatomic distances $d_{Cu(1)–Cu(2)}$, $d_{Cu(1)–TM}$, and $d_{Cu(2)–TM}$, vertical displacement $d_{TM–\beta\text{-}TBN}$, and binding energies E_b of Cu_2TM/β-TBN.

Cu_2TM/β-TBN	$d_{Cu(1)–Cu(2)}$ (Å)	$d_{Cu(1)–TM}$ (Å)	$d_{Cu(2)–TM}$ (Å)	$d_{TM–\beta\text{-}TBN}$ (Å)	E_b (eV)
Ti	2.94	2.12	2.12	1.67	–5.99
V	2.98	2.10	2.10	1.52	–5.32
Cr	3.13	2.10	2.10	1.54	–3.65
Mn	3.09	3.07	3.07	1.45	–3.46
Fe	2.65	2.75	2.75	0.15	–4.86
Co	2.67	2.80	2.80	0.07	–4.29
Ni	2.80	3.13	2.83	0.10	–4.25
Cu	2.53	2.31	2.31	0.94	–2.09
Zn	2.52	2.58	2.58	1.15	0.10
Zr	3.09	3.11	3.11	2.16	–6.47
Nb	3.23	3.17	3.17	2.13	–6.41
Mo	3.32	3.15	3.15	2.07	–6.62
Tc	3.24	3.18	2.83	1.86	–6.14
Ru	2.60	2.65	2.65	1.15	–4.91
Rh	2.54	2.62	2.63	0.70	–4.33
Pd	2.54	2.60	2.61	1.21	–2.36
Ag	2.53	2.73	2.73	0.97	–0.71
Cd	2.47	2.75	2.75	1.18	0.71

Table S2. Adsorption energies of $*CO_2$ in three different configurations on Cu_2TM/β-TBN.

Cu_2TM/β-TBN	$E_{ads}(*CO_2[1,2])$ (eV)	$E_{ads}(*CO_2[1,3])$ (eV)	$E_{ads}(*CO_2[2,3])$ (eV)
Ti	——	–0.54	–0.54
V	0.48	–0.43	–0.43
Cr	0.51	–0.16	–0.16
Mn	0.44	0.06	0.06
Fe	0.43	0.58	0.58
Co	0.23	0.44	0.44
Ni	0.23	0.12	0.16
Cu	0.69	0.65	0.65
Zr	——	–0.65	–0.65
Nb	——	–0.61	–0.61
Mo	0.32	–0.39	–0.39
Tc	0.29	0.00	0.27
Ru	——	–0.21	–0.21
Rh	0.11	0.04	0.04
Pd	0.59	0.29	0.29
Ag	0.39	0.51	0.51

Table S3. Magnetic moments of bare clusters and intermediate states.

Cu_2TM/β-TBN	Bare Clusters (μ_B)	Intermediate States (*CHOCO, μ_B)
Ti	0.762	0.248
V	2.451	2.021
Cr	3.718	2.983
Mn	3.897	2.505
Fe	2.871	1.486
Cu	0.000	0.248
Zr	0.000	0.000
Nb	0.000	0.000
Mo	1.901	0.000
Tc	1.628	0.114
Ru	0.393	0.212
Pd	0.000	0.000