

Supporting Information

A Theoretical Study on the Structural Evolution and Stability of Pt_xCu_y Heteronuclear Clusters Supported on $\text{t-ZrO}_2(101)$ Surface

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Catalogue

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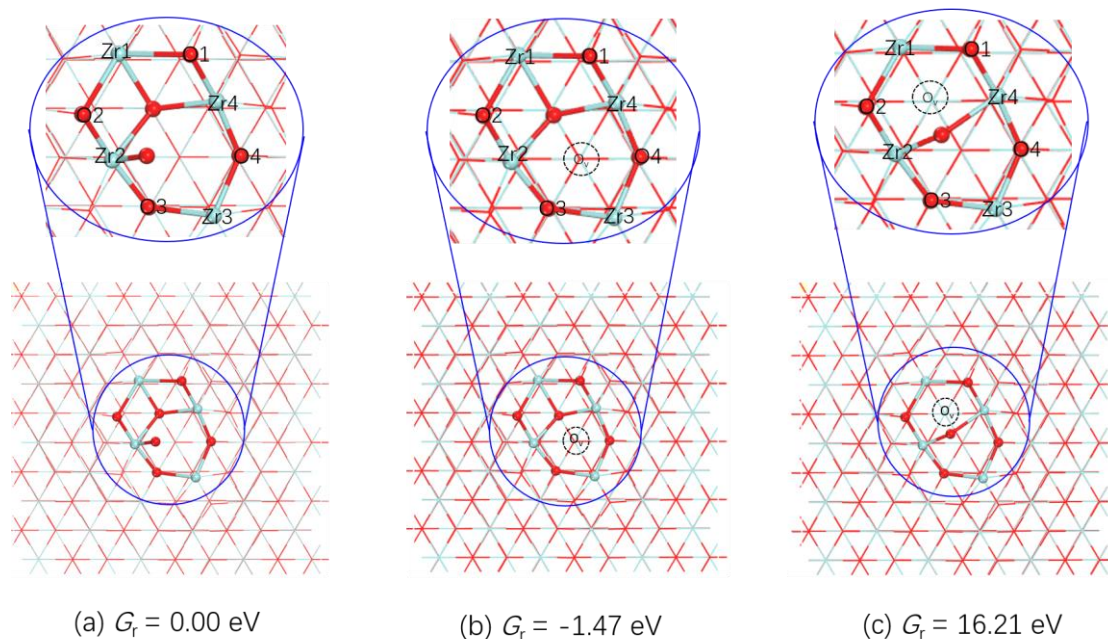


Figure S1 The relative Gibbs free energy (G_r) and top view of (a) t-ZrO₂(101); (b) t-ZrO₂(101)-Ov(O-3), (c) t-ZrO₂(101)-Ov(O4). “Ov” represents an oxygen vacancy.

Notes:

The calculation of G_r according to the following eq:

$$G_r = G(\text{Zr}_{120}\text{O}_{239}\text{-Ov}) - G(\text{Zr}_{120}\text{O}_{240}) + 1/2 G(^3\text{O}_2). \text{ (Reaction: } \text{Zr}_{120}\text{O}_{240} \rightarrow \text{Zr}_{120}\text{O}_{239}\text{-Ov} + 1/2 ^3\text{O}_2\text{).}$$

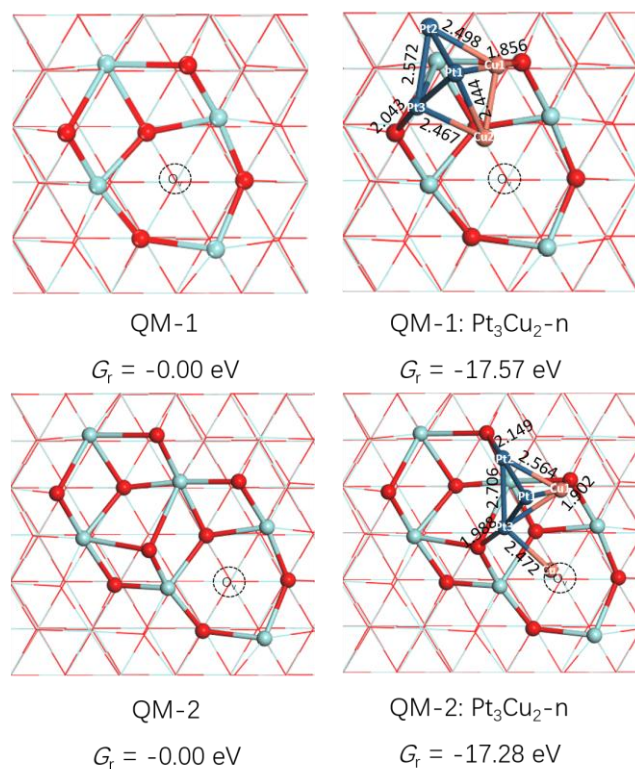


Figure S2 Selection of the QM region. “Ov” represents an oxygen vacancy.

Notes:

The QM region (QM-1): 4 Zr atoms, 5 O atoms and the Pt_xCu_y cluster.

the QM region (QM-2): 6 Zr atoms, 9 O atoms and the Pt_xCu_y cluster.

For instance, using the current approach (QM-1), the relative Gibbs free energy (G_r) for Pt₃Cu₂-n (Pt₃Cu₂/ZrO₂) was calculated to be -17.57 eV. With the newly extended QM region (QM-2), the corresponding G_r value was -17.28 eV. The difference between the two methods is only -0.29 eV, corresponding to a marginal relative error of just 1.6%. Consequently, we opted to retain the original QM region (QM-1) for subsequent calculations.

The calculation of G_r according to the following eq:

$$G_r = G(\text{Pt}_3\text{Cu}_2/\text{Zr}_{120}\text{O}_{239}\text{-Ov}) - G(\text{Zr}_{120}\text{O}_{239}\text{-Ov}) - 3G(^3\text{Pt}) - 2G(^2\text{Cu}).$$

$$(\text{Reaction: } \text{Zr}_{120}\text{O}_{239}\text{-Ov} + 3\ ^3\text{Pt} + 2\ ^2\text{Cu} \rightarrow \text{Pt}_3\text{Cu}_2/\text{Zr}_{120}\text{O}_{239}\text{-Ov}).$$

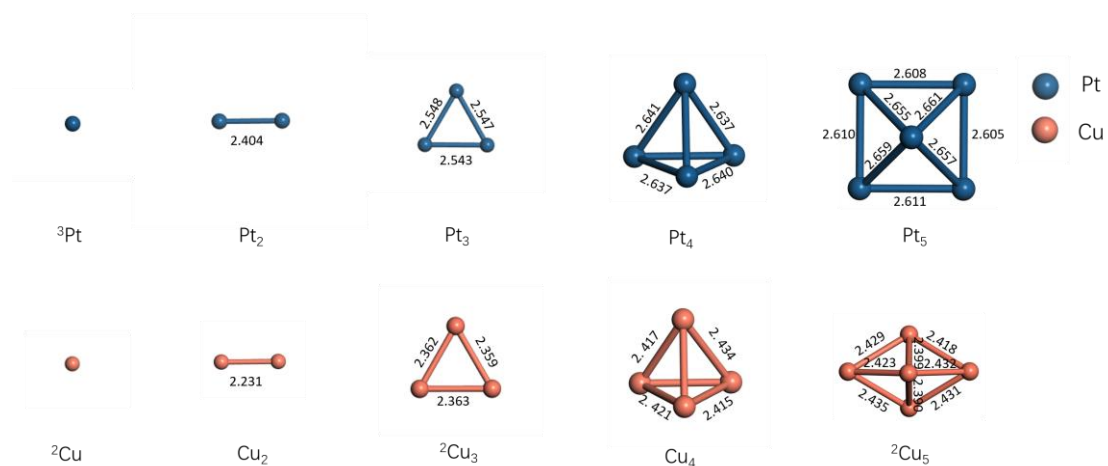


Figure S3 The most stable geometries of Pt_x and Cu_y (x, y = 1 ~ 5) clusters in the gas phase. The dark blue and orange atoms represent Pt and Cu, respectively. The superscript prefixes "2" and "3" are used to indicate the doublet and triplet state, respectively, while the default is denoted the singlet state. The black numbers represent distances (Å).

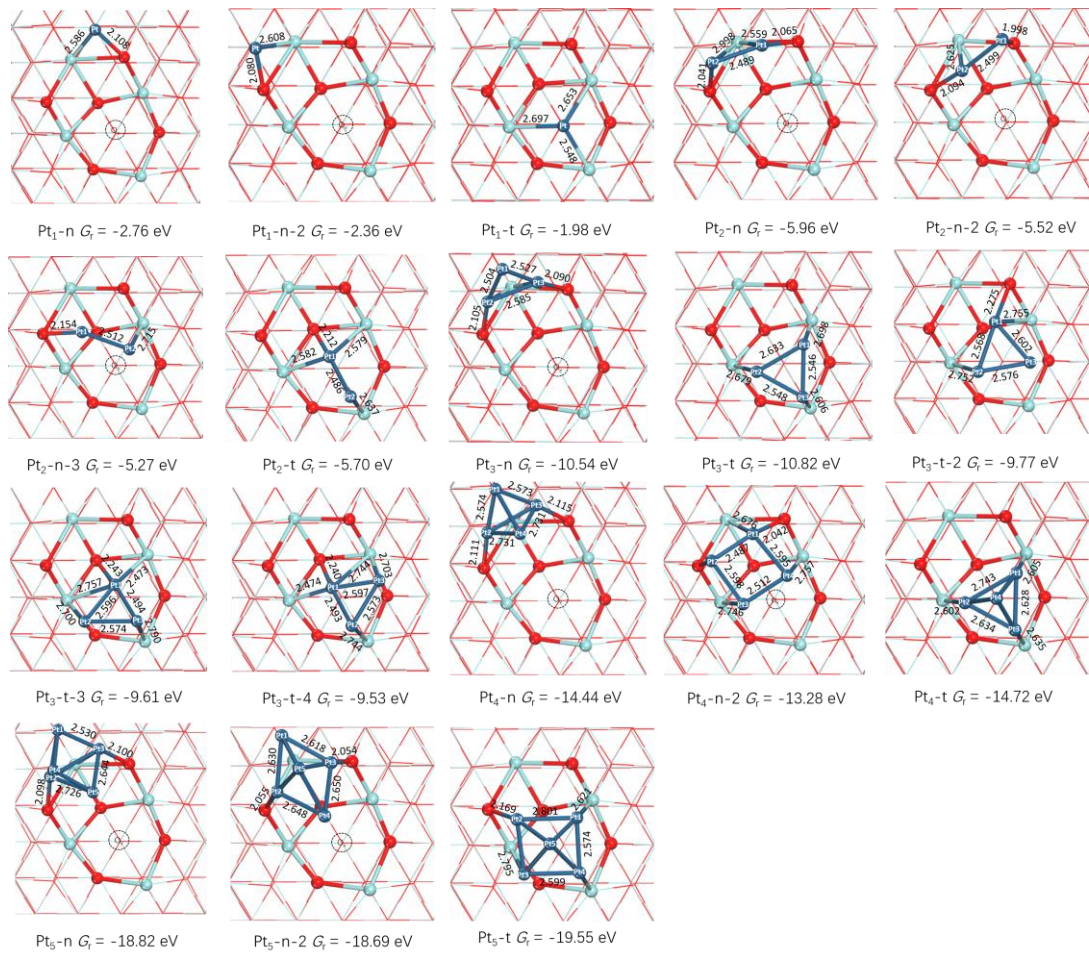


Figure S4 The geometries and relative Gibbs free energies (G_r) for Pt_x (x = 1 ~ 5) clusters on the t-ZrO₂(101) surface. The black numbers represent distances (Å).

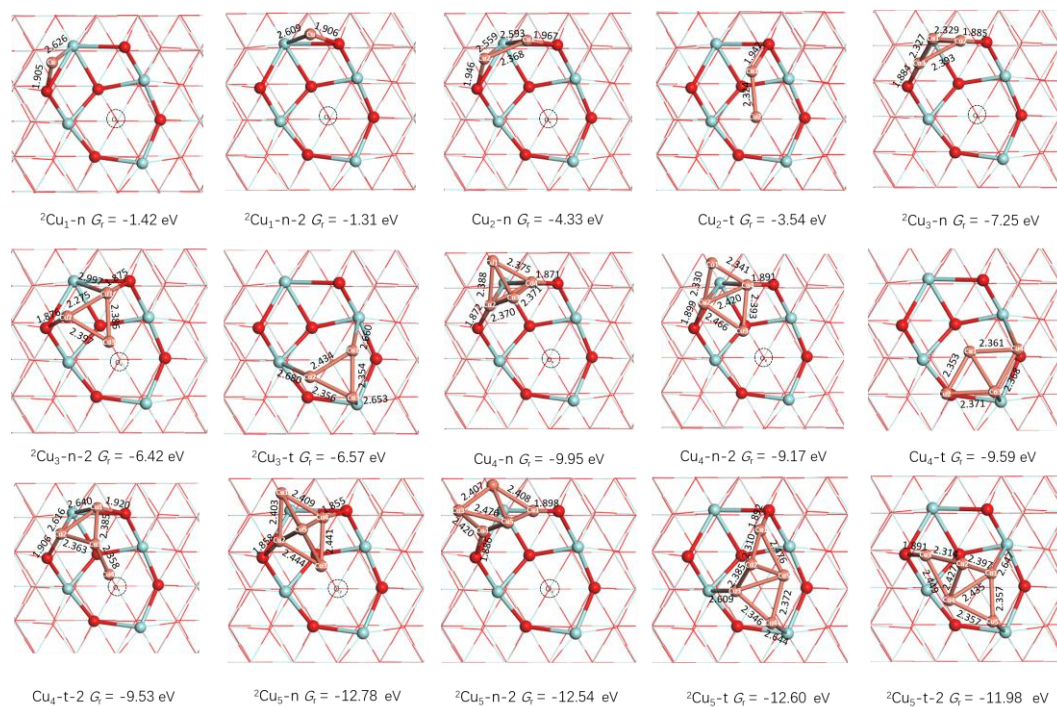


Figure S5 The geometries and relative Gibbs free energies (G_r) for Cu_y ($y = 1 \sim 5$) clusters on the $\text{t-ZrO}_2(101)$ surface. The superscript prefixes “2” is used to indicate the doublet state, while the default is denoted the singlet state. The black numbers represent distances (\AA).

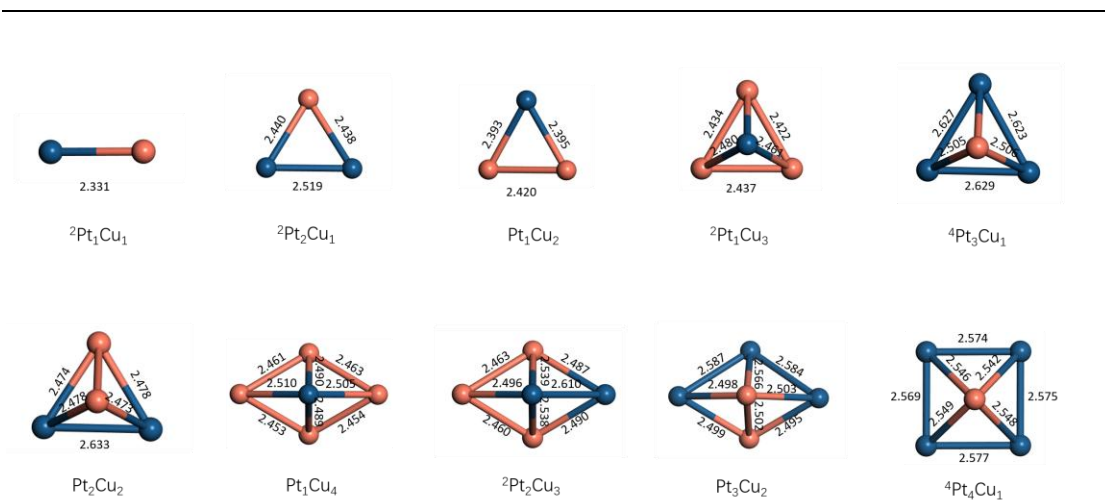


Figure S6 The most stable geometries of Pt_xCu_y ($x + y = 2 \sim 5$) clusters in the gas phase. The superscript prefixes "2" and "4" are used to indicate the doublet and quartet state, while the default is denoted the singlet state. The black numbers represent distances (\AA).

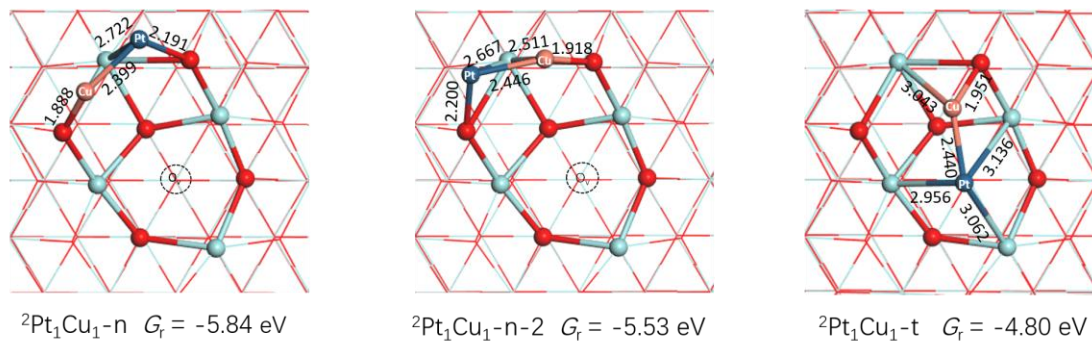


Figure S7 The geometries and relative Gibbs free energies (G_r) for Pt_1Cu_1 cluster on the t- $\text{ZrO}_2(101)$ surface. The superscript prefixes “2” is used to indicate the doublet state. The black numbers represent distances (Å).

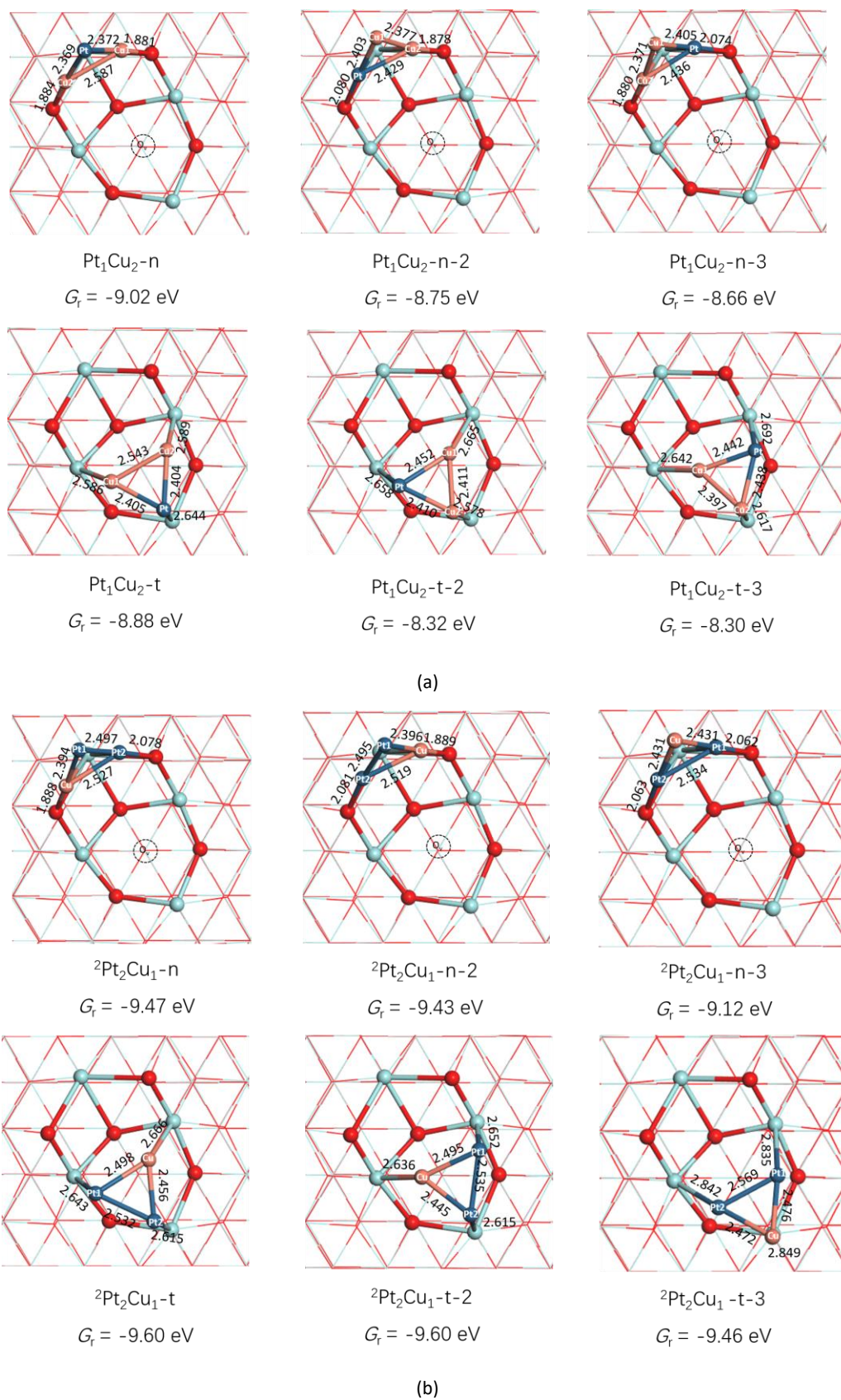
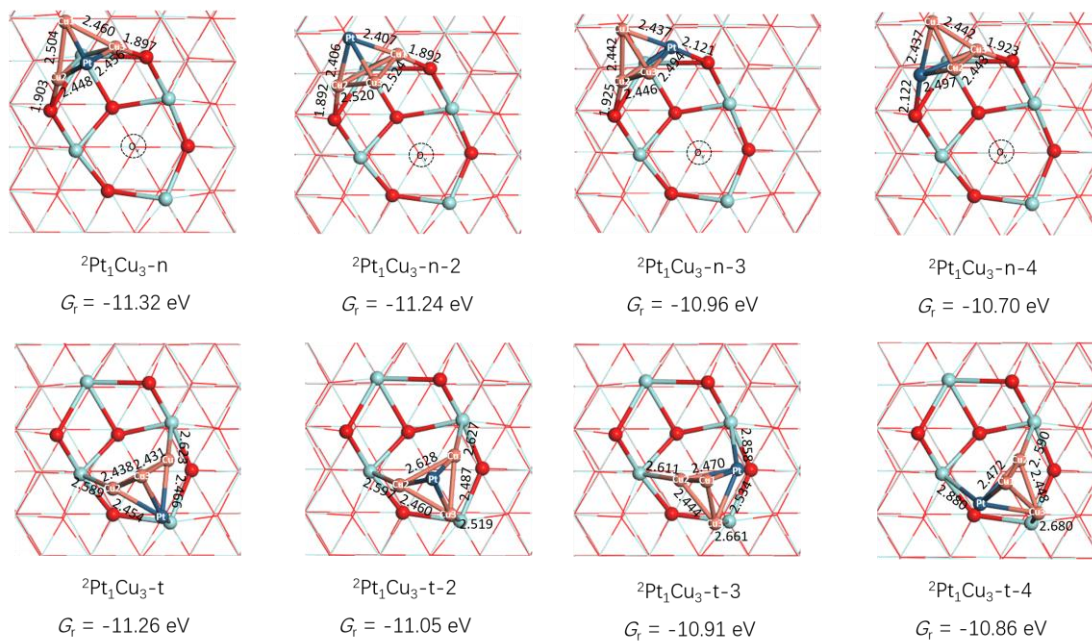
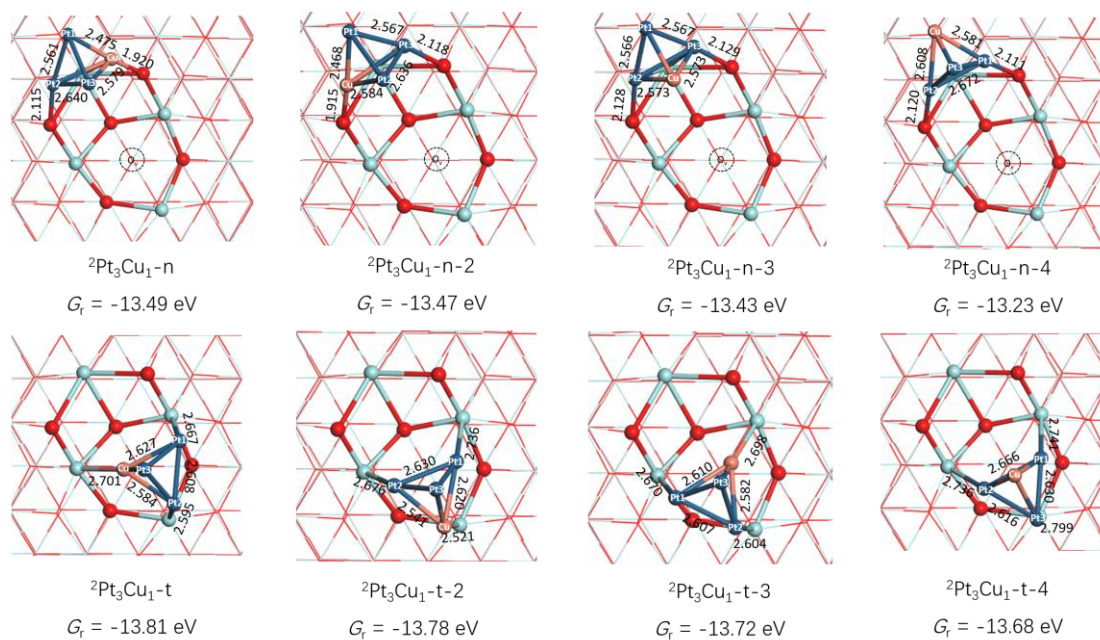


Figure S8 The geometries and relative Gibbs free energies (G_r) for Pt_xCu_y ($x + y = 3$) cluster on the t-ZrO₂(101) surface. The black numbers represent distances (Å). (a) Pt₁Cu₂/ZrO₂(101), (b)Pt₂Cu₁/ZrO₂(101).

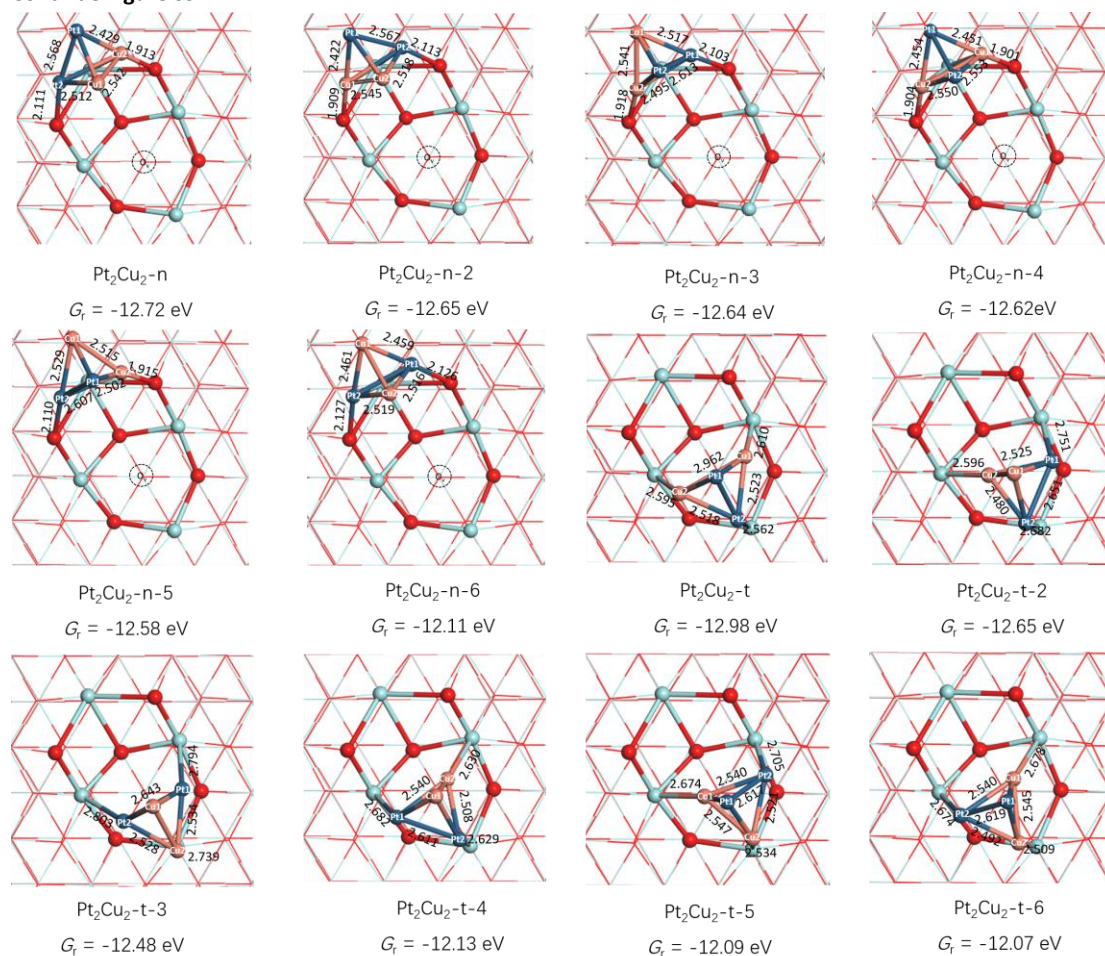


(a)



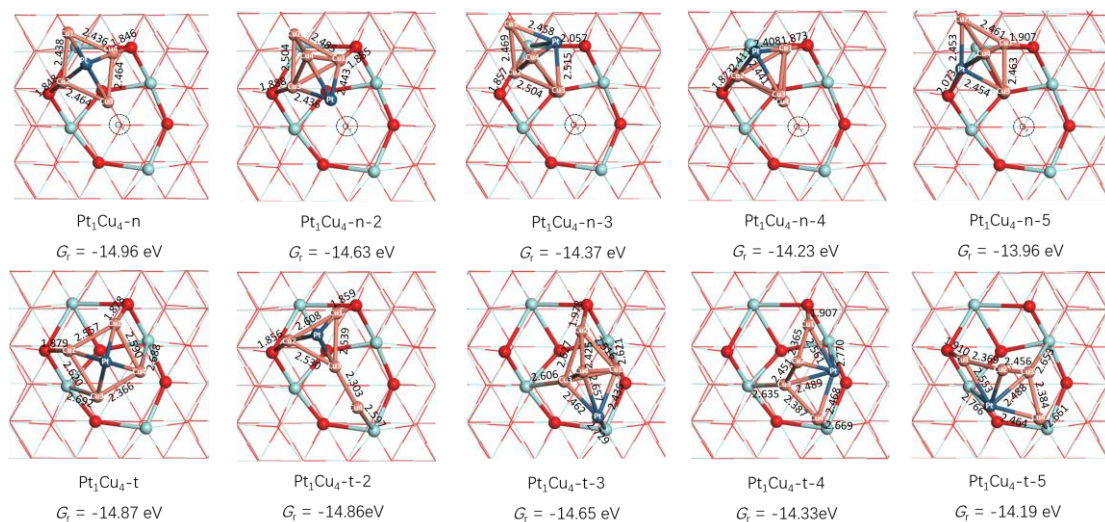
(b)

Continue Figure S9

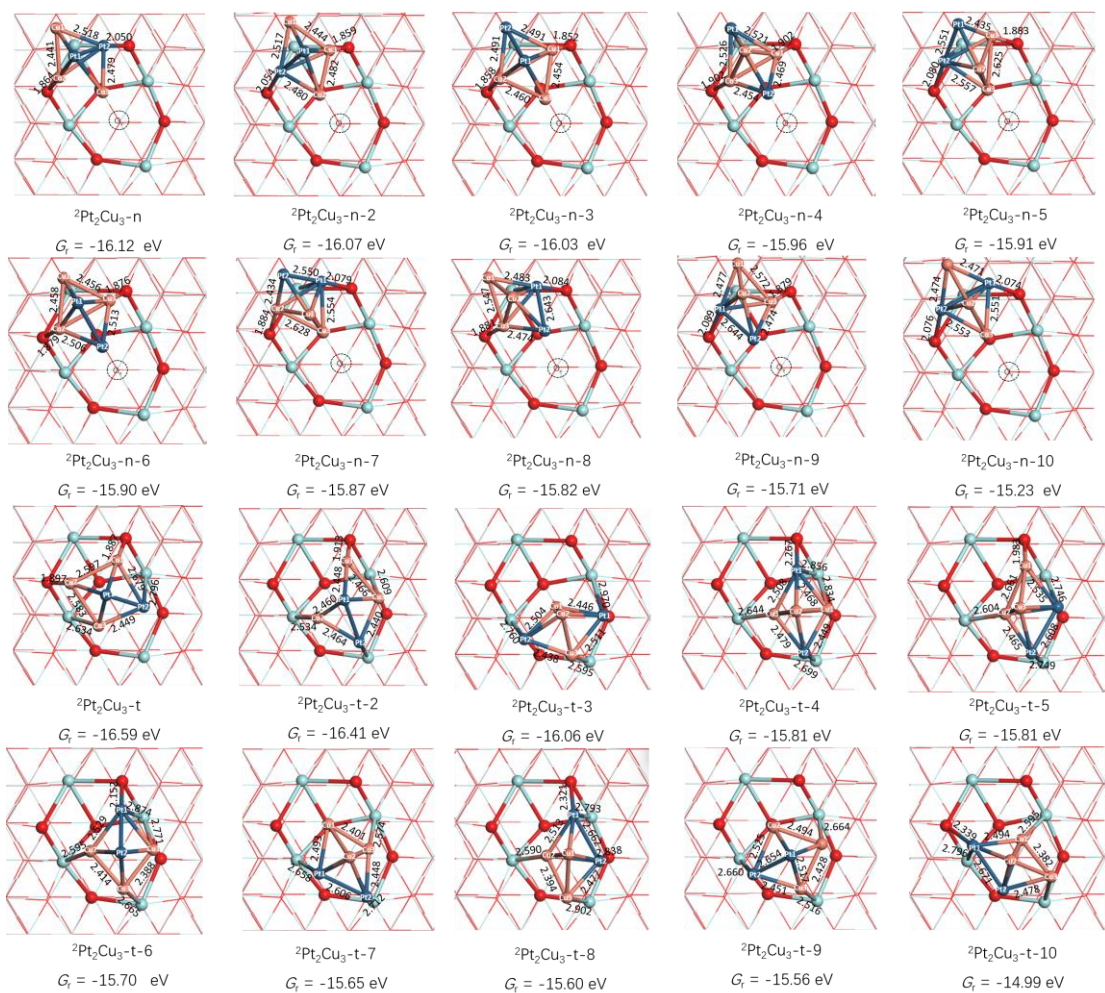


(c)

Figure S9 The geometries and relative Gibbs free energies (G_r) for Pt_xCu_y ($x + y = 4$) cluster on the t-ZrO₂(101) surface. (a)Pt₁Cu₃/ZrO₂(101), (b)Pt₃Cu₁/ZrO₂(101), (c) Pt₂Cu₂/ZrO₂(101). The superscript prefixes “2” is used to indicate the doublet state. The black numbers represent distances (Å).

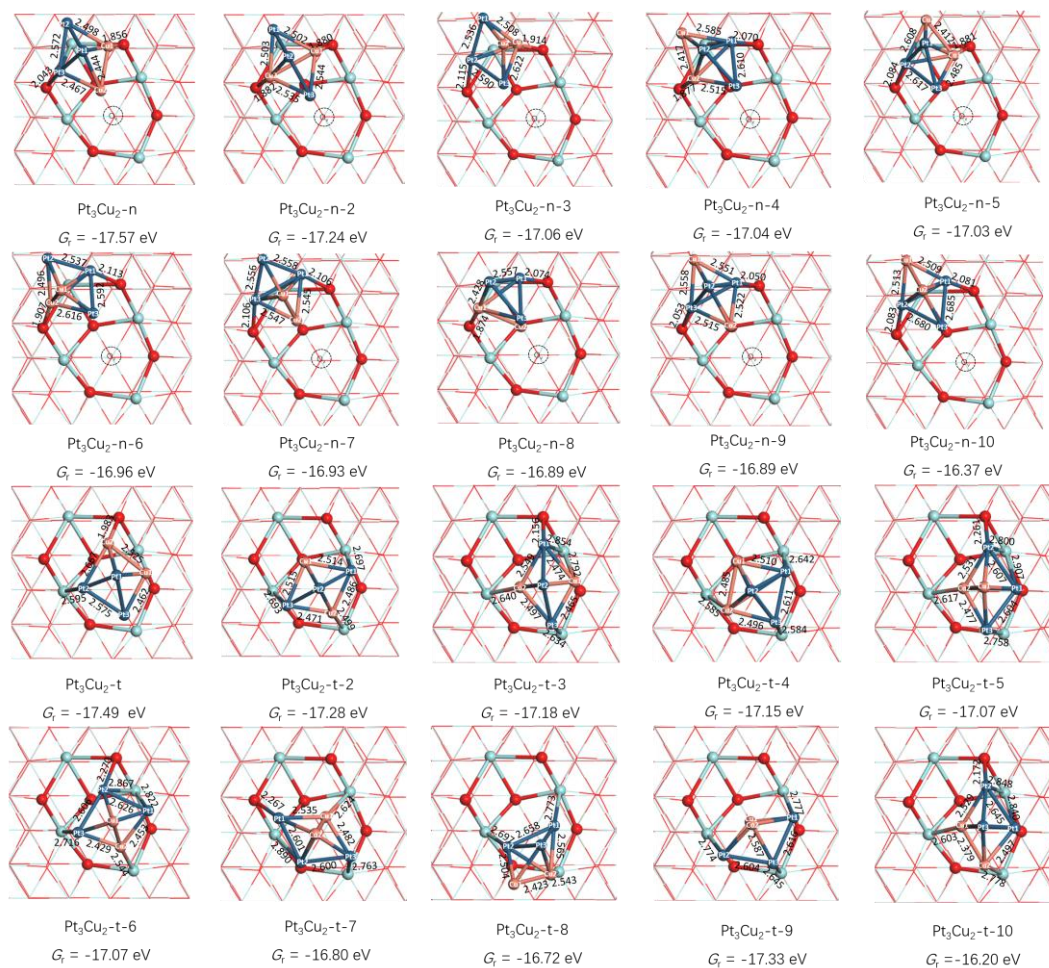


(a)

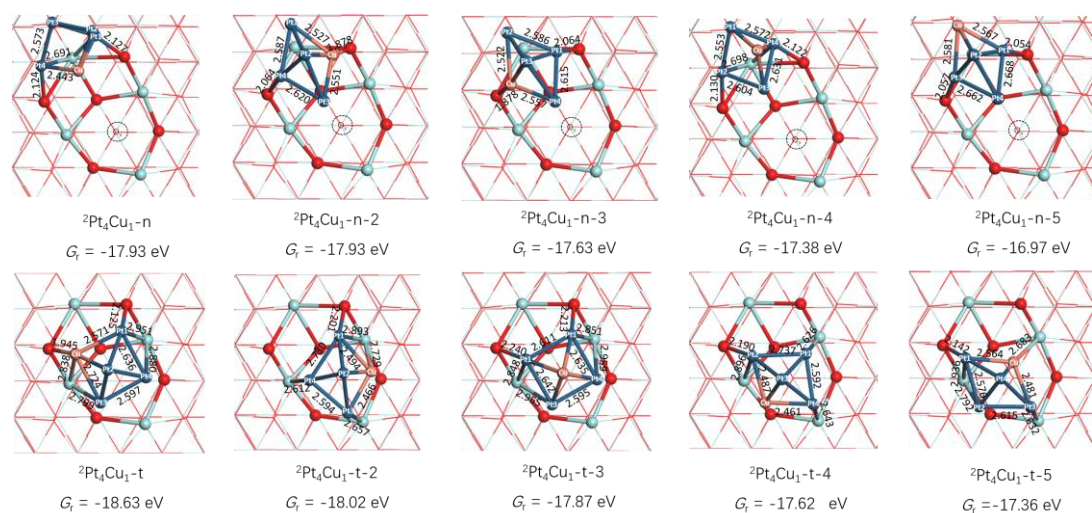


(b)

Continue Figure S10



(c)



(d)

Figure S10 The geometries and relative Gibbs free energies (G_r) for Pt_xCu_y ($x + y = 5$) cluster on the t-ZrO₂(101) surface. (a)Pt₁Cu₄/ZrO₂(101), (b)Pt₂Cu₃/ZrO₂(101), (c)Pt₃Cu₂/ZrO₂(101), (d)Pt₄Cu₁/ZrO₂(101). The superscript prefixes "2" is used to indicate the doublet state. The black numbers represent distances (Å).

Table S1. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t,g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and the relative Gibbs free energies (G_r , eV) of t-ZrO₂(101), t-ZrO₂(101)-Ov(O3), and t-ZrO₂(101)-Ov(O4).

Species	<i>ZPVE</i>	$E_{t,g}$	G_0	G_c	G_r
t-ZrO ₂ (101)	0.31112	-743.16627	0.13373	-743.03254	0.00
t-ZrO ₂ (101)-Ov(O-3)	0.30997	-668.07474	0.11374	-667.96099	-1.47
t-ZrO ₂ (101)-Ov(O-4)	0.30034	-667.43282	0.12074	-667.31208	16.21

Table S2. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t,g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and the relative Gibbs free energies (G_r , eV) of Pt_x and Cu_y ($x, y = 1 \sim 5$).

Species	multiplicity	<i>ZPVE</i>	$E_{t,g}$	G_0	G_c	G_r
Pt ₁	Triplet	0.00000	-195.21930	0.00000	0.00000	0.00
	Quintet	0.00000	-195.00483	0.00000	0.00000	5.84
Pt ₂	Singlet	0.00065	-390.55032	-0.01888	-390.56920	0.00
	Triplet	0.00065	-390.55017	-0.01888	-390.56906	0.00
Pt ₃	Singlet	0.00122	-585.88507	-0.02971	-585.91478	0.00
	Triplet	0.00121	-585.88443	-0.02986	-585.91429	0.01
Pt ₄	Singlet	0.00181	-781.21907	-0.04680	-781.26587	0.00
	Triplet	0.00181	-781.21906	-0.04678	-781.26584	0.00
Pt ₅	Singlet	0.00253	-976.56379	-0.07125	-976.63503	0.00
	Triplet	0.00253	-976.56187	-0.07139	-976.63327	0.05
Cu ₁	double	0.00000	-222.41593	0.00000	0.00000	0.00
	quartet	0.00000	-222.20241	0.00000	0.00000	5.81
Cu ₂	singlet	0.00102	-444.91179	-0.01466	-444.92645	0.00
	triplet	0.00072	-444.85698	-0.00852	-444.86550	1.66
Cu ₃	double	0.00180	-667.38270	-0.02150	-667.40419	0.00
	quartet	0.00216	-667.32961	-0.01841	-667.34802	1.53
Cu ₄	singlet	0.00289	-889.86414	-0.03363	-889.89777	0.00
	triplet	0.00287	-889.86372	-0.03370	-889.89742	0.00
Cu ₅	double	0.00331	-1112.38636	-0.04331	-1112.42967	0.00
	quartet	0.00387	-1112.36314	-0.04704	-1112.41018	0.53

Table S3. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t,g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and the relative Gibbs free energies (G_r , eV) of $\text{Pt}_x/\text{ZrO}_2(101)$ ($x = 1 \sim 5$).

Species	multiplicity	<i>ZPVE</i>	$E_{t,g}$	G_0	G_c	G_r
Pt_1/ZrO_2	Pt ₁ -n	0.31207	-863.38661	0.10500	-863.28162	-2.76
	Pt ₁ -n-2	0.31219	-863.38065	0.11359	-863.26706	-2.36
	Pt ₁ -t	0.31015	-863.36328	0.11025	-863.25302	-1.98
Pt_2/ZrO_2	Pt ₂ -n	0.31423	-1058.71334	0.09483	-1058.61851	-5.96
	Pt ₂ -n-2	0.31333	-1058.69987	0.09740	-1058.60247	-5.52
	Pt ₂ -n-3	0.30987	-1058.69417	0.10099	-1058.59317	-5.27
	Pt ₂ -t	0.31077	-1058.71123	0.10206	-1058.60916	-5.70
Pt_3/ZrO_2	Pt ₃ -n	0.31583	-1254.09092	0.08477	-1254.00615	-10.54
	Pt ₃ -t	0.31094	-1254.07753	0.06115	-1254.01638	-10.82
	Pt ₃ -t-2	0.31064	-1254.05769	0.07962	-1253.97807	-9.77
	Pt ₃ -t-3	0.31176	-1254.05609	0.08407	-1253.97202	-9.61
	Pt ₃ -t-4	0.31209	-1254.05714	0.08798	-1253.96915	-9.53
Pt_4/ZrO_2	Pt ₄ -n	0.31689	-1449.42642	0.05745	-1449.36896	-14.44
	Pt ₄ -n-2	0.31420	-1449.39396	0.06773	-1449.32623	-13.28
	Pt ₄ -t	0.31223	-1449.42589	0.04685	-1449.37903	-14.72
Pt_5/ZrO_2	Pt ₅ -n	0.31759	-1644.78567	0.03639	-1644.74928	-18.82
	Pt ₅ -n-2	0.31748	-1644.78607	0.04174	-1644.74433	-18.69
	Pt ₅ -t	0.31320	-1644.80696	0.03114	-1644.77582	-19.55

Table S4. The binding energies (G_{BE} , eV), the clusters deformation energies ($\Delta G_{def,Pt_x}$, eV), the t-ZrO₂ (101) deformation energies ($\Delta G_{def,ZrO_2}$, eV), the metal-metal bond energy ($\Delta G_{bond,Pt_x}$, eV), the metal-support interaction energies (G_{MS} , eV), the nucleation energies (G_{nuc} , eV), and the charge transfer (ET) for the most stable configurations of Pt_x/ZrO₂(101) ($x = 1 \sim 5$).

Configuration	Species	G_{BE}	$\Delta G_{def,Pt_x}$	$\Delta G_{def,ZrO_2}$	$\Delta G_{bond,Pt_x}$	G_{MS}	G_{nuc}	ET
Pt ₁ /ZrO ₂	Pt ₁ -n	-2.76	0.00	0.52	0.00	-3.27	0.00	0.119
	Pt ₁ -t	-1.98	0.00	0.91	0.00	-2.89	0.00	-0.089
Pt ₂ /ZrO ₂	Pt ₂ -n	-2.98	0.06	0.77	-1.78	-1.97	-0.44	-0.001
	Pt ₂ -t	-2.85	0.05	0.99	-1.78	-2.07	-0.19	-0.032
Pt ₃ /ZrO ₂	Pt ₃ -n	-3.51	0.08	0.70	-2.33	-1.88	-1.82	-0.08
	Pt ₃ -t	-3.61	-0.17	0.04	-2.33	-1.32	-2.36	0.128
Pt ₄ /ZrO ₂	Pt ₄ -n	-3.61	0.39	0.85	-2.64	-1.82	-1.15	0.045
	Pt ₄ -t	-3.68	-0.01	-0.01	-2.64	-1.03	-1.14	0.049
Pt ₅ /ZrO ₂	Pt ₅ -n	-3.76	0.28	0.82	-2.93	-1.65	-1.62	0.028
	Pt ₅ -t	-3.91	0.24	0.12	-2.93	-1.10	-2.07	0.049

Table S5. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t,g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and the relative Gibbs free energies (G_r , eV) of $\text{Cu}_y/\text{ZrO}_2(101)$ ($y = 1 \sim 5$).

Species	multiplicity	<i>ZPVE</i>	$E_{t,g}$	G_0	G_c	G_r
Cu_1/ZrO_2	$\text{Cu}_1\text{-n}$	0.31233	-890.54549	0.11651	-890.42898	-1.42
	$\text{Cu}_1\text{-n-2}$	0.31218	-890.54005	0.11502	-890.42503	-1.31
Cu_2/ZrO_2	$\text{Cu}_2\text{-n}$	0.31539	-1113.05716	0.10516	-1112.95201	-4.33
	$\text{Cu}_2\text{-t}$	0.31090	-1113.02325	0.10044	-1112.92281	-3.54
Cu_3/ZrO_2	$\text{Cu}_3\text{-n}$	0.31524	-1335.56015	0.08484	-1335.47531	-7.25
	$\text{Cu}_3\text{-n-2}$	0.31450	-1335.54049	0.09578	-1335.44472	-6.42
	$\text{Cu}_3\text{-t}$	0.31206	-1335.53036	0.08015	-1335.45021	-6.57
Cu_4/ZrO_2	$\text{Cu}_4\text{-n}$	0.31766	-1558.07292	0.08267	-1557.99025	-9.95
	$\text{Cu}_4\text{-n-2}$	0.31781	-1558.04506	0.08333	-1557.96173	-9.17
	$\text{Cu}_4\text{-t}$	0.31266	-1558.04574	0.06869	-1557.97705	-9.59
	$\text{Cu}_4\text{-t-2}$	0.31688	-1558.05004	0.07516	-1557.97488	-9.53
Cu_5/ZrO_2	$\text{Cu}_5\text{-n}$	0.31776	-1780.57604	0.06572	-1780.51032	-12.78
	$\text{Cu}_5\text{-n-2}$	0.31878	-1780.57230	0.07097	-1780.50133	-12.54
	$\text{Cu}_5\text{-t}$	0.31428	-1780.56122	0.05764	-1780.50358	-12.60
	$\text{Cu}_5\text{-t-2}$	0.31471	-1780.54978	0.06879	-1780.48098	-11.98

Table S6. The binding energies (G_{BE} , eV), the clusters deformation energies ($\Delta G_{def,Cu_y}$, eV), the t-ZrO₂(101) deformation energies ($\Delta G_{def,ZrO_2}$, eV), the metal-metal bond energy ($\Delta G_{bond,Cu_y}$, eV), the metal-support interaction energies (G_{MS} , eV), the nucleation energies (G_{nuc} , eV), and the charge transfer (ET) for the most stable configurations of Cu_y/ZrO₂(101) ($y = 1 \sim 5$).

Configuration	Species	G_{BE}	$\Delta G_{def,Cu_y}$	$\Delta G_{def,ZrO_2}$	$\Delta G_{bond,Cu_y}$	G_{MS}	G_{nuc}	ET
Cu ₁ /ZrO ₂	Cu ₁ -n	-1.42	0.00	0.85	0.00	-2.26	0.00	0.173
Cu ₂ /ZrO ₂	Cu ₂ -n	-2.17	0.04	0.96	-1.29	-1.84	-1.50	0.257
	Cu ₂ -t	-1.77	0.13	0.87	-1.29	-1.35	-0.70	0.132
Cu ₃ /ZrO ₂	Cu ₃ -n	-2.42	0.10	1.08	-1.42	-2.08	-1.51	0.312
	Cu ₃ -t	-2.19	-0.24	-0.04	-1.42	-0.73	-1.62	0.201
Cu ₄ /ZrO ₂	Cu ₄ -n	-2.49	0.19	0.84	-1.59	-1.74	-1.28	0.394
	Cu ₄ -t	-2.40	-0.57	0.21	-1.59	-1.02	-1.60	0.225
Cu ₅ /ZrO ₂	Cu ₅ -n	-2.56	-0.10	0.95	-1.90	-1.60	-1.42	0.250
	Cu ₅ -t	-2.52	0.17	0.53	-1.90	-1.15	-1.59	0.228

Table S7. Zero-point vibrational energies (*ZPVE*, hartree), sum of electronic energies in the gas phase ($E_{t,g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and the relative Gibbs free energies (G_r , eV) of Pt_xCu_y ($x + y = 2 \sim 5$) clusters in the gas phase.

Species	multiplicity	<i>ZPVE</i>	$E_{t,g}$	G_0	G_c	G_r
Pt ₁ Cu ₁	double	0.00061	-417.73087	-0.01232	-417.74320	0.00
	quartet	0.00055	-417.67738	-0.00996	-417.68734	1.52
Pt ₂ Cu ₁	double	0.00149	-613.06326	-0.03544	-613.09870	0.00
	quartet	0.00150	-613.04220	-0.03482	-613.07702	0.59
Pt ₁ Cu ₂	singlet	0.00151	-640.23379	-0.02580	-640.25959	0.00
	triplet	0.00116	-640.21271	-0.01086	-640.22357	0.98
Pt ₃ Cu ₁	double	0.00207	-808.39944	-0.03319	-808.43263	0.00
	quartet	0.00196	-808.38838	-0.04615	-808.43454	-0.05
Pt ₁ Cu ₃	double	0.00240	-862.72592	-0.05147	-862.77739	0.00
	quartet	0.00241	-862.69685	-0.03840	-862.73524	1.15
Pt ₂ Cu ₂	singlet	0.00232	-835.57160	-0.04231	-835.61392	0.00
	triplet	0.00229	-835.56139	-0.04170	-835.60309	0.29
Pt ₁ Cu ₄	singlet	0.00347	-1085.23644	-0.05410	-1085.29055	0.00
	triplet	0.00335	-1085.23222	-0.04292	-1085.27514	0.42
Pt ₂ Cu ₃	double	0.00303	-1058.08163	-0.04897	-1058.13059	0.00
	quartet	0.00322	-1058.06828	-0.05699	-1058.12528	0.14
Pt ₃ Cu ₂	singlet	0.00327	-1030.93191	-0.05414	-1030.98605	0.00
	triplet	0.00328	-1030.93023	-0.05442	-1030.98465	0.04
Pt ₄ Cu ₁	double	0.00285	-1003.74621	-0.06011	-1003.80633	0.00
	quartet	0.00289	-1003.74847	-0.05962	-1003.80810	-0.05

Table S8. Zero-point vibrational energies (ZPVE, hartree), sum of electronic energies in the gas phase ($E_{t,g}$, hartree), thermal correction to Gibbs free energies (G_0 , hartree), sum of electronic and thermal Gibbs free energies (G_c , hartree) and the relative Gibbs free energies (G_r , eV) of Pt_xCu_y/ZrO_2 ($x + y = 2 \sim 5$).

Species	multiplicity	ZPVE	$E_{t,g}$	G_0	G_c	G_r
Pt ₁ Cu ₁ /ZrO ₂	Pt ₁ Cu ₁ -n	0.31475	-1085.90255	0.09156	-1085.81099	-5.84
	Pt ₁ Cu ₁ -n-2	0.31472	-1085.90151	0.10204	-1085.79948	-5.53
	Pt ₁ Cu ₁ -t	0.31033	-1085.87217	0.09939	-1085.77278	-4.80
Pt ₁ Cu ₂ /ZrO ₂	Pt ₁ Cu ₂ -n	0.31677	-1308.43117	0.08753	-1308.34364	-9.02
	Pt ₁ Cu ₂ -n-2	0.31625	-1308.42066	0.08693	-1308.33373	-8.75
	Pt ₁ Cu ₂ -n-3	0.31630	-1308.42002	0.08954	-1308.33048	-8.66
	Pt ₁ Cu ₂ -t	0.31170	-1308.41202	0.07362	-1308.33840	-8.88
	Pt ₁ Cu ₂ -t-2	0.31181	-1308.40411	0.08637	-1308.31773	-8.32
	Pt ₁ Cu ₂ -t-3	0.31180	-1308.40442	0.08719	-1308.31723	-8.30
	Pt ₂ Cu ₁ /ZrO ₂	Pt ₂ Cu ₁ -n	0.31612	-1281.24815	0.08474	-1281.16341
Pt ₂ Cu ₁ -n-2	0.31613	-1281.24591	0.08398	-1281.16193	-9.43	
Pt ₂ Cu ₁ -n-3	0.31611	-1281.23539	0.08456	-1281.15083	-9.12	
Pt ₂ Cu ₁ -t	0.31123	-1281.24182	0.07336	-1281.16846	-9.60	
Pt ₂ Cu ₁ -t-2	0.31132	-1281.24143	0.07317	-1281.16826	-9.60	
Pt ₂ Cu ₁ -t-3	0.31116	-1281.23991	0.07659	-1281.16332	-9.46	
Pt ₁ Cu ₃ /ZrO ₂	Pt ₁ Cu ₃ -n	0.31708	-1530.92188	0.07763	-1530.84425	-11.32
	Pt ₁ Cu ₃ -n-2	0.31763	-1530.92282	0.08150	-1530.84131	-11.24
	Pt ₁ Cu ₃ -n-3	0.31685	-1530.90294	0.07224	-1530.83069	-10.96
	Pt ₁ Cu ₃ -n-4	0.31693	-1530.90333	0.08208	-1530.82125	-10.70
	Pt ₁ Cu ₃ -t	0.31280	-1530.90373	0.06180	-1530.84192	-11.26
	Pt ₁ Cu ₃ -t-2	0.31297	-1530.89643	0.06237	-1530.83405	-11.05
	Pt ₁ Cu ₃ -t-3	0.31250	-1530.90147	0.07259	-1530.82888	-10.91
	Pt ₁ Cu ₃ -t-4	0.31253	-1530.89901	0.07177	-1530.82724	-10.86
	Pt ₃ Cu ₁ /ZrO ₂	Pt ₃ Cu ₁ -n	0.31709	-1476.59827	0.06781	-1476.53045
Pt ₃ Cu ₁ -n-2	0.31712	-1476.59797	0.06811	-1476.52985	-13.47	
Pt ₃ Cu ₁ -n-3	0.31674	-1476.59735	0.06884	-1476.52851	-13.43	
Pt ₃ Cu ₁ -n-4	0.31657	-1476.58683	0.06594	-1476.52090	-13.23	
Pt ₃ Cu ₁ -t	0.31259	-1476.59431	0.05197	-1476.54234	-13.81	
Pt ₃ Cu ₁ -t-2	0.31260	-1476.60238	0.06097	-1476.54141	-13.78	
Pt ₃ Cu ₁ -t-3	0.31234	-1476.60557	0.06647	-1476.53910	-13.72	
Pt ₃ Cu ₁ -t-4	0.31200	-1476.59438	0.05692	-1476.53746	-13.68	
Pt ₂ Cu ₂ /ZrO ₂	Pt ₂ Cu ₂ -n	0.31702	-1503.76544	0.06644	-1503.69900	-12.72
	Pt ₂ Cu ₂ -n-2	0.31716	-1503.76549	0.06903	-1503.69646	-12.65
	Pt ₂ Cu ₂ -n-3	0.31685	-1503.76122	0.06531	-1503.69591	-12.64
	Pt ₂ Cu ₂ -n-4	0.31749	-1503.77170	0.07645	-1503.69526	-12.62
	Pt ₂ Cu ₂ -n-5	0.31696	-1503.76114	0.06723	-1503.69390	-12.58
	Pt ₂ Cu ₂ -n-6	0.31680	-1503.74664	0.07006	-1503.67658	-12.11
	Pt ₂ Cu ₂ -t	0.31320	-1503.77339	0.06482	-1503.70857	-12.98

Continue Table S8

Species	multiplicity	ZPVE	$E_{t,g}$	G_0	G_c	G_r
	Pt ₂ Cu ₂ -t-2	0.31246	-1503.76636	0.07012	-1503.69625	-12.65
	Pt ₂ Cu ₂ -t-3	0.31243	-1503.75430	0.06426	-1503.69004	-12.48
	Pt ₂ Cu ₂ -t-4	0.31233	-1503.75412	0.07700	-1503.67712	-12.13
	Pt ₂ Cu ₂ -t-5	0.31283	-1503.74506	0.06915	-1503.67591	-12.09
	Pt ₂ Cu ₂ -t-6	0.31287	-1503.74556	0.07066	-1503.67490	-12.07
Pt ₁ Cu ₄	Pt ₁ Cu ₄ -n	0.31806	-1753.45559	0.06178	-1753.39382	-14.96
	Pt ₁ Cu ₄ -n-2	0.31657	-1753.44502	0.06348	-1753.38153	-14.63
	Pt ₁ Cu ₄ -n-3	0.31844	-1753.43840	0.06622	-1753.37218	-14.37
	Pt ₁ Cu ₄ -n-4	0.31822	-1753.43364	0.06676	-1753.36688	-14.23
	Pt ₁ Cu ₄ -n-5	0.31811	-1753.42184	0.06496	-1753.35688	-13.96
	Pt ₁ Cu ₄ -t	0.31598	-1753.45699	0.06656	-1753.39043	-14.87
	Pt ₁ Cu ₄ -t-2	0.31667	-1753.44561	0.05564	-1753.38997	-14.86
	Pt ₁ Cu ₄ -t-3	0.31403	-1753.44017	0.05762	-1753.38255	-14.65
	Pt ₁ Cu ₄ -t-4	0.31396	-1753.43389	0.06321	-1753.37068	-14.33
	Pt ₁ Cu ₄ -t-5	0.31436	-1753.42169	0.05638	-1753.36531	-14.19
Pt ₂ Cu ₃	Pt ₂ Cu ₃ -n	0.31805	-1726.29197	0.05205	-1726.23991	-16.12
	Pt ₂ Cu ₃ -n-2	0.31816	-1726.29243	0.05442	-1726.23800	-16.07
	Pt ₂ Cu ₃ -n-3	0.31779	-1726.28928	0.05293	-1726.23634	-16.03
	Pt ₂ Cu ₃ -n-4	0.31609	-1726.29426	0.06043	-1726.23383	-15.96
	Pt ₂ Cu ₃ -n-5	0.31797	-1726.28654	0.05440	-1726.23214	-15.91
	Pt ₂ Cu ₃ -n-6	0.31669	-1726.29515	0.06344	-1726.23170	-15.90
	Pt ₂ Cu ₃ -n-7	0.31804	-1726.28630	0.05571	-1726.23059	-15.87
	Pt ₂ Cu ₃ -n-8	0.31734	-1726.27735	0.04849	-1726.22886	-15.82
	Pt ₂ Cu ₃ -n-9	0.31777	-1726.27787	0.05320	-1726.22466	-15.71
	Pt ₂ Cu ₃ -n-10	0.31774	-1726.26902	0.06192	-1726.20710	-15.23
	Pt ₂ Cu ₃ -t	0.31502	-1726.30813	0.05098	-1726.25715	-16.59
	Pt ₂ Cu ₃ -t-2	0.31450	-1726.30063	0.05032	-1726.25031	-16.41
	Pt ₂ Cu ₃ -t-3	0.31300	-1726.29205	0.05441	-1726.23764	-16.06
	Pt ₂ Cu ₃ -t-4	0.31327	-1726.28074	0.05222	-1726.22852	-15.81
	Pt ₂ Cu ₃ -t-5	0.31340	-1726.28440	0.05605	-1726.22835	-15.81
	Pt ₂ Cu ₃ -t-6	0.31392	-1726.27250	0.04811	-1726.22439	-15.70
	Pt ₂ Cu ₃ -t-7	0.31304	-1726.28000	0.05732	-1726.22269	-15.65
	Pt ₂ Cu ₃ -t-8	0.31275	-1726.27175	0.05121	-1726.22054	-15.60
	Pt ₂ Cu ₃ -t-9	0.31347	-1726.27462	0.05539	-1726.21924	-15.56
	Pt ₂ Cu ₃ -t-10	0.31292	-1726.25796	0.05962	-1726.19834	-14.99
Pt ₃ Cu ₂	Pt ₃ Cu ₂ -n	0.31785	-1699.13564	0.03937	-1699.09627	-17.57
	Pt ₃ Cu ₂ -n-2	0.31709	-1699.14159	0.05720	-1699.08439	-17.24
	Pt ₃ Cu ₂ -n-3	0.31788	-1699.12795	0.05025	-1699.07770	-17.06
	Pt ₃ Cu ₂ -n-4	0.31754	-1699.12710	0.05008	-1699.07703	-17.04

Continue Table S8

Species	multiplicity	ZPVE	$E_{t,g}$	G_0	G_c	G_r
	Pt ₃ Cu ₂ -n-5	0.31747	-1699.12799	0.05125	-1699.07674	-17.03
	Pt ₃ Cu ₂ -n-6	0.31810	-1699.12725	0.05317	-1699.07408	-16.96
	Pt ₃ Cu ₂ -n-7	0.31779	-1699.12661	0.05362	-1699.07299	-16.93
	Pt ₃ Cu ₂ -n-8	0.31811	-1699.12306	0.05174	-1699.07131	-16.89
	Pt ₃ Cu ₂ -n-9	0.31814	-1699.12636	0.05485	-1699.07151	-16.89
	Pt ₃ Cu ₂ -n-10	0.31783	-1699.10544	0.05314	-1699.05230	-16.37
	Pt ₃ Cu ₂ -t	0.31385	-1699.14189	0.04834	-1699.09355	-17.49
	Pt ₃ Cu ₂ -t-2	0.31323	-1699.13360	0.04772	-1699.08588	-17.28
	Pt ₃ Cu ₂ -t-3	0.31367	-1699.13763	0.05547	-1699.08215	-17.18
	Pt ₃ Cu ₂ -t-4	0.31320	-1699.13027	0.04918	-1699.08109	-17.15
	Pt ₃ Cu ₂ -t-5	0.31285	-1699.13126	0.05320	-1699.07805	-17.07
	Pt ₃ Cu ₂ -t-6	0.31299	-1699.12035	0.04237	-1699.07797	-17.07
	Pt ₃ Cu ₂ -t-7	0.31292	-1699.12851	0.06039	-1699.06811	-16.80
	Pt ₃ Cu ₂ -t-8	0.31346	-1699.11011	0.04481	-1699.06529	-16.72
	Pt ₃ Cu ₂ -t-9	0.31316	-1699.14201	0.05422	-1699.08779	-17.33
	Pt ₃ Cu ₂ -t-10	0.31327	-1699.09968	0.05343	-1699.04625	-16.20
Pt ₄ Cu ₁	Pt ₄ Cu ₁ -n	0.31746	-1671.96340	0.05030	-1671.91310	-17.93
	Pt ₄ Cu ₁ -n-2	0.31723	-1671.94690	0.03389	-1671.91301	-17.93
	Pt ₄ Cu ₁ -n-3	0.31718	-1671.94677	0.04487	-1671.90189	-17.63
	Pt ₄ Cu ₁ -n-4	0.31767	-1671.94534	0.05255	-1671.89279	-17.38
	Pt ₄ Cu ₁ -n-5	0.31775	-1671.92478	0.04699	-1671.87779	-16.97
	Pt ₄ Cu ₁ -t	0.31369	-1671.98172	0.04285	-1671.93887	-18.63
	Pt ₄ Cu ₁ -t-2	0.31318	-1671.96096	0.04461	-1671.91634	-18.02
	Pt ₄ Cu ₁ -t-3	0.31291	-1671.96408	0.05323	-1671.91085	-17.87
	Pt ₄ Cu ₁ -t-4	0.31345	-1671.94706	0.04542	-1671.90165	-17.62
	Pt ₄ Cu ₁ -t-5	0.31318	-1671.94957	0.05757	-1671.89200	-17.36

Table S9. The binding energies (G_{BE} , eV), the clusters deformation energies ($\Delta G_{\text{def,Pt}_x\text{Cu}_y}$, eV), the t-ZrO₂(101) deformation energies ($\Delta G_{\text{def,ZrO}_2}$, eV), the metal-metal bond energy ($\Delta G_{\text{bond,Pt}_x\text{Cu}_y}$, eV), the metal-support interaction energies (G_{MS} , eV), the nucleation energies (G_{nuc} , eV), and the charge transfer (ET) for the most stable configurations of Pt_xCu_y/ZrO₂(101) ($x + y = 2 \sim 5$).

Configuration	Species	G_{BE}	$\Delta G_{\text{def,Pt}_x\text{Cu}_y}$	$\Delta G_{\text{def,ZrO}_2}$	$\Delta G_{\text{bond,Pt}_x\text{Cu}_y}$	G_{MS}	G_{nuc}	ET
Pt ₁ Cu ₁ /ZrO ₂	Pt ₁ Cu ₁ -n	-2.92	0.27	1.03	-1.47	-2.48	-1.67	0.114
	Pt ₁ Cu ₁ -t	-2.40	0.06	1.16	-1.47	-2.09	-0.63	0.036
Pt ₁ Cu ₂ /ZrO ₂	Pt ₁ Cu ₂ -n	-3.01	0.19	0.83	-1.89	-1.95	-1.76	0.100
	Pt ₁ Cu ₂ -t	-2.96	0.20	0.09	-1.89	-1.16	-2.66	0.135
Pt ₂ Cu ₁ /ZrO ₂	Pt ₂ Cu ₁ -n	-3.16	0.25	0.80	-2.21	-1.74	-0.87	-0.014
	Pt ₂ Cu ₁ -t	-3.20	0.18	0.12	-2.21	-1.10	-2.04	0.141
Pt ₁ Cu ₃ /ZrO ₂	Pt ₁ Cu ₃ -n	-2.83	0.24	0.83	-2.11	-1.55	-0.89	0.294
	Pt ₁ Cu ₃ -t	-2.82	0.56	-0.06	-2.11	-0.64	-0.97	0.157
Pt ₃ Cu ₁ /ZrO ₂	Pt ₃ Cu ₁ -n	-3.37	0.23	1.35	-2.45	-2.27	-1.26	0.187
	Pt ₃ Cu ₁ -t	-3.45	0.00	0.27	-2.45	-1.27	-1.45	0.122
Pt ₂ Cu ₂ /ZrO ₂	Pt ₂ Cu ₂ -n	-3.18	0.51	1.05	-2.34	-1.89	-1.84	0.279
	Pt ₂ Cu ₂ -t	-3.25	0.54	0.10	-2.34	-1.01	-1.96	0.091
Pt ₁ Cu ₄ /ZrO ₂	Pt ₁ Cu ₄ -n	-2.99	0.30	0.90	-2.22	-1.67	-2.22	0.226
	Pt ₁ Cu ₄ -t	-2.97	-0.16	0.94	-2.22	-1.69	-2.19	0.262
Pt ₂ Cu ₃ /ZrO ₂	Pt ₂ Cu ₃ -n	-3.22	0.45	0.87	-2.42	-1.68	-1.98	0.275
	Pt ₂ Cu ₃ -t	-3.32	0.11	1.01	-2.42	-1.91	-2.19	0.150
Pt ₃ Cu ₂ /ZrO ₂	Pt ₃ Cu ₂ -n	-3.51	0.75	0.86	-2.70	-1.67	-2.09	0.074
	Pt ₃ Cu ₂ -t	-3.50	0.55	0.37	-2.70	-1.16	-2.53	0.203
Pt ₄ Cu ₁ /ZrO ₂	Pt ₄ Cu ₁ -n	-3.59	0.00	0.90	-2.80	-1.68	-1.69	0.137
	Pt ₄ Cu ₁ -t	-3.73	-0.16	0.76	-2.80	-1.68	-2.84	0.199