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

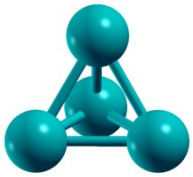
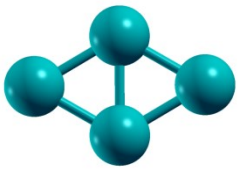
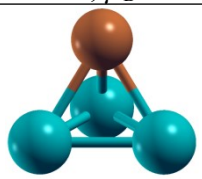
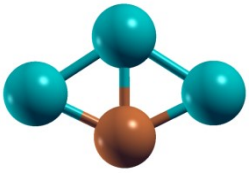
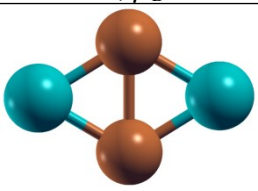
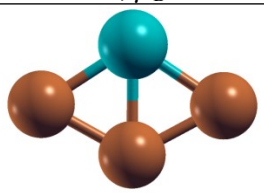
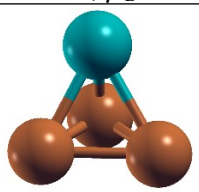
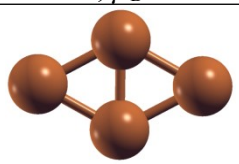
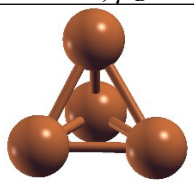
ST1: Binding energy (E_b) and related bond lengths of H_2, H, 2H, CO_2, HOCO, HCOO and HCOOH on Pd_4Cu_4 cluster.

Adsorbate species	Site	Bond lengths (Å)	E_b (eV)
H_2	Top Cu	Cu-H = 1.68, 1.68, H-H= 0.83	-4.91
H	Mid of Pd-Pd-Cu triangle	Cu-H=1.81, Pd-H = 1.75	-2.87
2H	Cu-Pd, Pd-Pd bridge	Cu-H = 1.82, Pd-H = 1.76	-5.87
CO_2	Cu-Pd edge	Cu-O=1.93, Pd-C=1.98, C-O = 1.25, 1.23	-0.96
HCOO	Carboxyl (Cu-Pd edge)	Pd-O=1.99, Cu-C=1.99, C-O=1.27, 1.35, O-H=0.99	-2.44
	Bidentate (Cu-Pd edge)	Cu-O=1.91, Pd-O=2.09, C-O=1.27, C-H=1.11	-3.67
HCOOH	Cu-Pd edge trans	Cu-O=1.93, C-O=1.25, 1.31, C-H=1.10, O-H=1.08	-1.17

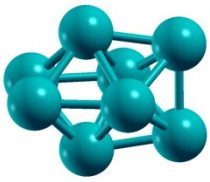
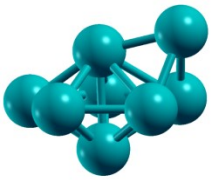
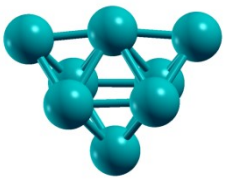
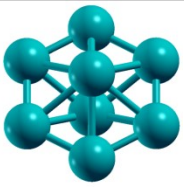
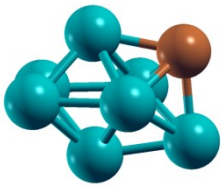
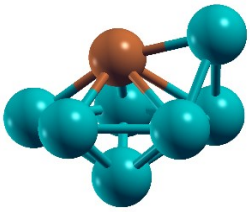
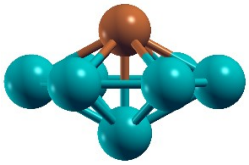
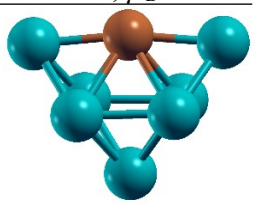
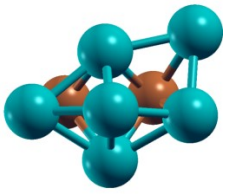
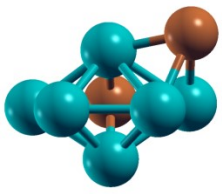
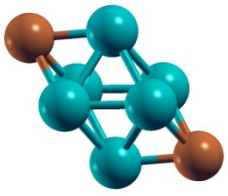
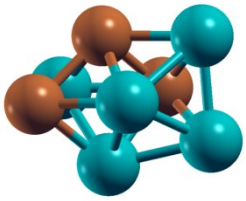
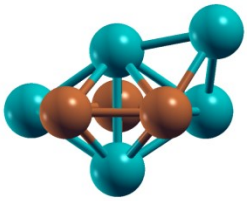
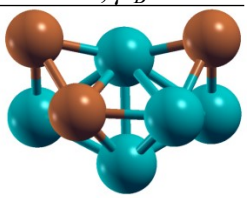
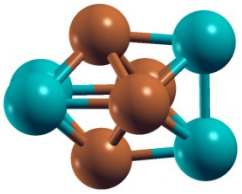
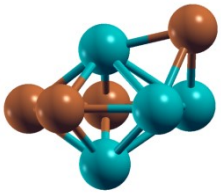
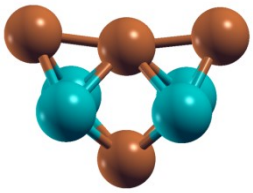
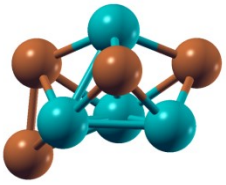
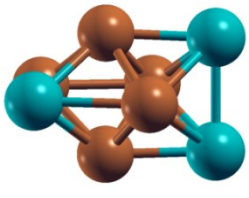
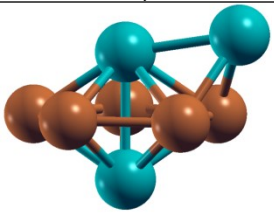
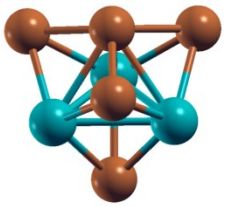
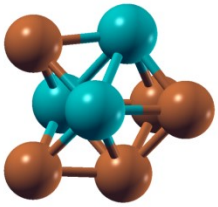
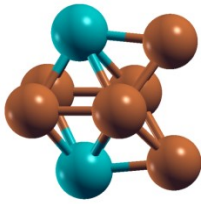
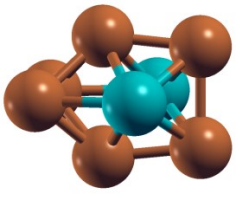
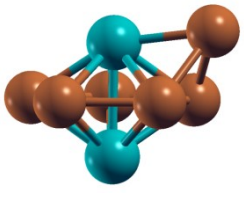
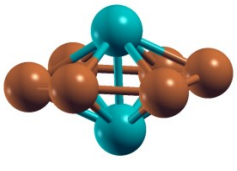
ST2: Binding energy (E_b) and related bond lengths of H_2, H, 2H, CO_2, HOCO, HCOO and HCOOH on $Pd_{12}Cu$ cluster.

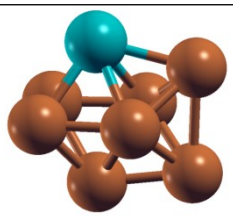
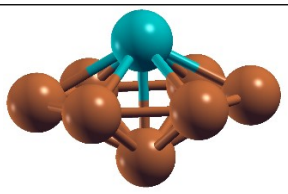
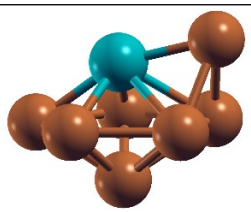
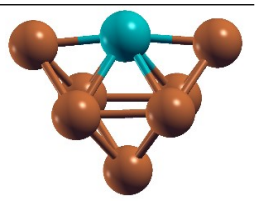
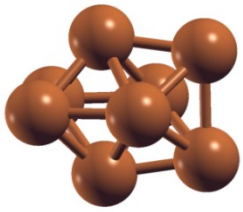
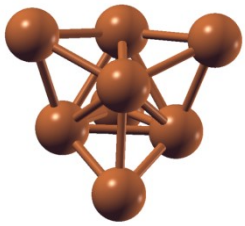
Adsorbate species	Site	Bond lengths (Å)	E_b (eV)
H_2	Top-Pd	Pd-H = 1.70, H-H=0.88	-5.06
H	Mid of 3-Pd triangle	Pd-H (average) = 1.83	-2.85
2H	fcc, hcp	Pd-H (average) = 1.83	-5.13
CO_2	Pd-Pd edge	C-O = 1.27	-0.44
HCOO	Carboxyl	Pd-O=2.26, Pd-C= 1.96, C-O=1.25, 1.35, O-H= 0.99	-2.50
	Bidentate	Pd-O = 2.10	-3.22
HCOOH	atop-trans	Pd-H= 2.16, Pd-O= 2.19	-0.90
	atop-cis	Pd-O= 2.13	-0.47

ST3: Geometric isomers of Pd_4, Pd_mCu_n (m+n = 4) and Cu_4 clusters (Atomic colours: Green = Pd, Brown= Cu)

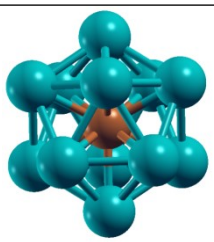
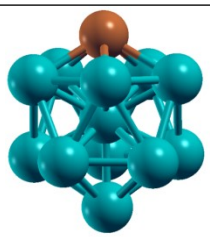
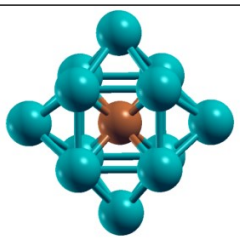
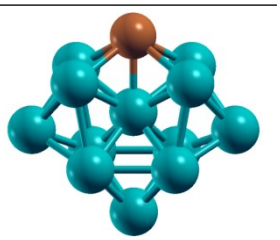
Cluster		
Pd_4		
	ΔE=0, μ_B = 0	0.84 eV, μ_B = 2.0
Pd_3Cu		
	ΔE=0, μ_B = 1.0	0.62 eV, μ_B = 1.0
Pd_2Cu_2		
	ΔE=0, μ_B = 0	0.40 eV, μ_B = 1.0
$PdCu_3$		
	ΔE=0, μ_B = 1.0	0.28 eV, μ_B = 1
Cu_4		
	ΔE=0, μ_B = 0	0.17 eV, μ_B = 4

ST4: Geometric isomers of Pd_8, Pd_mCu_n (m+n = 8) and Cu_8 clusters (Atomic colours: Green = Pd, Brown= Cu)

Clusters				
Pd_8				
	ΔE=0, μ_B = 2.0	0.17 eV, μ_B = 4.0	0.41 eV, μ_B = 4.0	0.98 eV, μ_B = 2.0
Pd_7Cu				
	ΔE=0, μ_B = 3.0	0.08 eV, μ_B = 1.0	0.19 eV, μ_B = 1.0	0.68eV, μ_B = 1.0
Pd_6Cu_2				
	ΔE=0, μ_B = 2.0	0.04 eV, μ_B = 2.0	0.09 eV, μ_B = 2.0	0.05eV, μ_B = 2.0
Pd_5Cu_3				
	ΔE=0, μ_B = 1.0	0.12 eV, μ_B = 3.0	0.27 eV, μ_B = 1.0	0.44 eV, μ_B = 1.0
Pd_4Cu_4				
	ΔE=0, μ_B = 0	0.16 eV, μ_B = 0	0.32 eV, μ_B = 0	0.36 eV, μ_B = 0
Pd_3Cu_5				
	ΔE=0, μ_B = 1.0	0.03 eV, μ_B = 1.0	0.73 eV, μ_B = 3.0	0.36 eV, μ_B = 1.0
Pd_2Cu_6				
	ΔE=0, μ_B = 2.0	0.08 eV, μ_B = 0	0.28 eV, μ_B = 0	0.34 eV, μ_B = 0

$PdCu_7$				
	ΔE=0, μ_B = 1.0	0.23 eV, μ_B = 0	0.71 eV, μ_B = 1.0	0.92 eV, μ_B = 1.0
Cu_8				
	ΔE=0, μ_B = 0	0.41 eV, μ_B = 1.0		

ST5: Geometric isomers of $Pd_{12}Cu$ cluster (Atomic colours: Green = Pd, Brown= Cu)

Cluster				
$CuPd_{12}$				
	ΔE=0, μ_B = 7.0	0.67 eV, μ_B = 7.0	0.79 eV, μ_B = 3.0	0.98 eV, μ_B = 3.0

ST6: Total Charge distribution (e/Å^3) on atoms of Pd_2Cu_2 and CO_2 adsorbed Pd_2Cu_2 cluster (Pd_2Cu_2-CO_2).

Atom(s)	Charges on atom(s)		
	Pd_2Cu_2-CO_2	Pd_2Cu_2	CO_2
Pd	8.635	8.601	-
Cu	9.865	9.895	-
C	2.576	-	2.738
^{1}O	5.136	-	5.174
^{2}O	5.126	-	5.174

ST7: Total Charge distribution (e/Å^3) on atoms of Pd_4Cu_4 and CO_2 adsorbed Pd_4Cu_4 cluster (Pd_4Cu_4-CO_2).

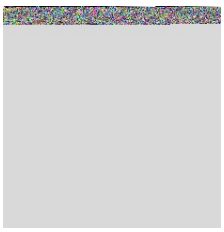
Atom(s)	Charges on atom(s)		
	Pd_4Cu_4-CO_2	Pd_4Cu_4	CO_2
Pd	8.628	8.570	-
Cu	9.925	9.935	-
C	2.571	-	2.738
^{1}O	5.148	-	5.174
^{2}O	5.122	-	5.174

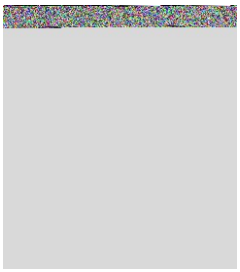
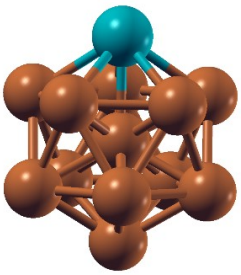
ST8: Total Charge distribution (e/Å^3) on atoms of $Pd_{12}Cu$ and CO_2 adsorbed $Pd_{12}Cu$ cluster ($Pd_{12}Cu$-CO_2).

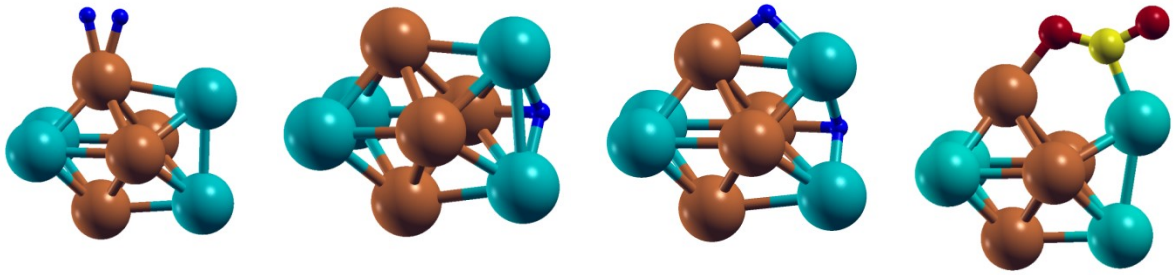
Atom(s)	Charges on atom(s)		
	$Pd_{12}Cu$-CO_2	$Pd_{12}Cu$	CO_2
^{1}Pd	8.607	8.519	-
^{2}Pd	8.490	8.518	-
C	2.579	-	2.738
^{1}O	5.115	-	5.174
^{2}O	5.131	-	5.174

ST9: Lowest energy Pd_4, Cu_4, Pd_8, Cu_8 and Pd_mCu_n (m+n=4, 8 and 13) clusters along with their position coordinates (in cartesian). (Atomic colours: Green: Pd, Brown: Cu)

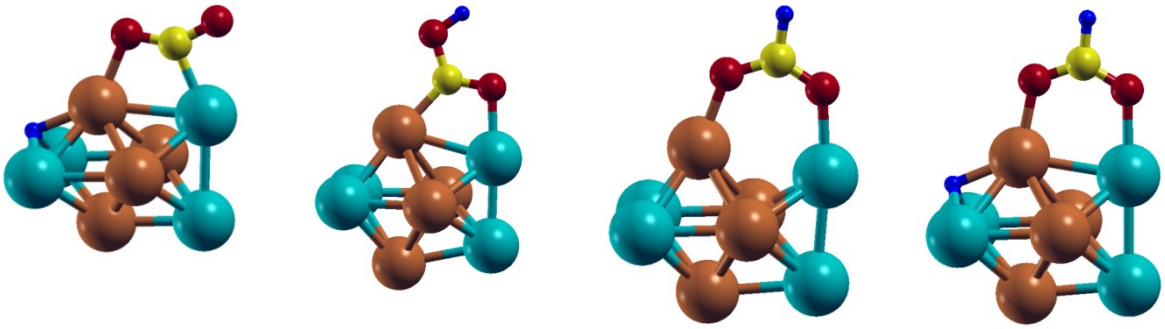
Clusters	Position Coordinates		
Pd_4	**Pd**- 6.20251	6.12697	5.98625
	Pd- 7.50000	6.95381	8.09590
	Pd- 8.79749	6.12697	5.98625
	Pd- 7.50000	8.39224	5.93160
Pd_3Cu	**Pd**- 6.01340	7.83309	7.42878
	Pd- 8.45272	7.18420	8.04100
	Pd- 7.56843	6.78497	5.63018
	Cu- 7.96545	9.09774	6.50003
Pd_2Cu_2	**Pd**- 8.72362	7.15486	8.45678
	Pd- 7.83528	8.37877	6.21727
	Cu- 6.51011	8.23543	8.29506
	Cu- 6.93099	6.23094	7.03088
$PdCu_3$	**Pd**- 6.68959	7.44084	6.49181
	Cu- 8.24688	7.56627	8.40523
	Cu- 8.63225	5.96243	6.75607
	Cu- 6.43129	9.03046	8.34690
Cu_4	**Cu**- 6.62695	6.29374	7.80640
	Cu- 8.48451	7.69360	8.28994
	Cu- 7.36693	7.70436	6.20141
	Cu- 5.52161	6.30830	5.70226
Pd_8	**Pd**- 8.81324	6.77398	6.47819
	Pd- 6.59289	9.70497	8.18016
	Pd- 8.18472	5.44078	8.70057
	Pd- 8.60808	8.07988	8.81770
	Pd- 6.52655	5.40779	6.58966
	Pd- 6.10810	7.10982	8.60172
	Pd- 6.47079	8.03763	6.10306
	Pd- 8.69563	9.44515	6.52895
Pd_7Cu	**Pd**- 6.90848	8.32846	6.01817
	Pd- 8.88630	5.49787	8.09746
	Pd- 7.50608	7.52202	9.24752
	Pd- 9.23568	8.02794	7.31180
	Pd- 6.38617	6.06386	7.34713
	Pd- 5.26472	8.40938	8.12589
	Pd- 7.45621	9.91858	8.09695
	Cu- 8.35631	6.23189	5.75507

Pd_6Cu_2		**Pd**- 6.77541 9.44874 8.95674 **Pd**- 8.18187 7.11632 9.18920 **Pd**- 5.57706 7.10248 8.88411 **Pd**- 7.11295 5.82844 7.07225 **Pd**- 6.07648 8.27347 6.58985 **Pd**- 8.60157 8.69009 7.14200 **Cu**- 9.56061 6.37369 6.96397 **Cu**- 8.11405 7.16677 5.20187
Pd_5Cu_3		**Pd-** 8.81877 7.85736 8.53291 **Pd-** 6.88288 9.66018 8.27939 **Pd-** 6.28316 7.39941 9.46839 **Pd-** 8.09753 8.64818 6.05234 **Pd-** 7.16935 6.26554 5.21993 **Cu**- 7.42179 5.96482 7.69701 **Cu**- 9.38163 6.49705 6.36020 **Cu**- 5.94489 7.70746 6.98280
Pd_4Cu_4		**Pd-** 8.41260 7.92226 5.98272 **Pd-** 7.93875 5.73626 7.46418 **Pd-** 7.78237 9.10548 8.30146 **Pd-** 5.86473 7.23836 8.25101 **Cu**- 7.96559 6.97405 9.70201 **Cu**- 9.71494 7.43797 8.13828 **Cu**- 6.21850 6.63323 5.79294 **Cu**- 6.10251 8.95241 6.36741
Pd_3Cu_5		**Pd-** 7.42083 6.74278 9.60487 **Pd-** 8.59003 9.30884 6.11515 **Pd-** 7.89276 5.14057 7.61385 **Cu**- 9.18575 7.37052 7.82416 **Cu**- 7.20951 8.70742 8.08701 **Cu**- 5.89423 6.76766 7.52878 **Cu**- 6.09631 8.76469 5.96623 **Cu**- 7.71092 6.99752 5.96444
Pd_2Cu_6		**Pd-** 7.99816 6.46347 5.73313 **Pd-** 7.28180 6.94462 9.48003 **Cu**- 8.50203 8.19026 7.58512 **Cu**- 6.76765 9.32523 8.83677 **Cu**- 9.03284 5.85196 7.97663 **Cu**- 7.42775 8.91034 5.55147 **Cu**- 6.23223 7.62405 7.21386 **Cu**- 6.75755 5.29008 7.62301

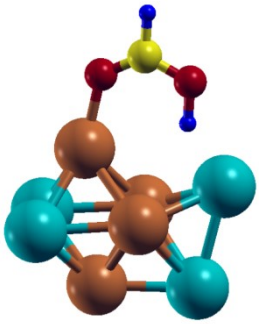
$PdCu_7$		**Pd-** 8.92577	8.58022	6.71933
		Cu- 8.63939	8.49900	9.30242
		Cu- 8.11453	6.36047	5.70694
		Cu- 6.51053	6.83008	9.50951
		Cu- 6.63235	8.24058	5.60879
		Cu- 6.70429	8.61040	7.94138
		Cu- 6.10681	6.37896	7.15812
		Cu- 8.36631	6.50028	8.05351
Cu_8		**Cu-** 8.52566	7.57742	8.78501
		Cu- 6.21939	7.39252	9.32180
		Cu- 7.15900	5.89039	7.67838
		Cu- 9.32222	6.39725	6.83513
		Cu- 7.41793	7.50311	5.85105
		Cu- 9.12149	8.89424	6.85353
		Cu- 5.33759	7.31452	6.98900
		Cu- 6.89670	9.03070	7.68607
$Pd_{12}Cu$		**Pd-** 7.25354	6.85560	7.18362
		Pd- 7.25586	6.85368	9.92225
		Pd- 9.86312	6.83318	10.76432
		Pd- 11.46824	6.82151	8.55291
		Pd- 9.86131	6.83980	6.33818
		Pd- 6.79286	4.53178	8.55049
		Pd- 8.40561	4.51821	10.76415
		Pd- 11.00326	4.49227	9.91505
		Pd- 11.00155	4.49882	7.18024
		Pd- 8.40255	4.52550	6.33022
		Pd- 9.14766	8.27986	8.55420
		Pd- 9.10481	3.07354	8.54428
		Cu- 9.12964	5.67625	8.55007
$PdCu_{12}$		**Pd-** 10.96320	4.57673	9.86335
		Cu- 9.13468	5.67425	8.55189
		Cu- 7.40207	6.71592	7.31354
		Cu- 7.37194	6.74277	9.82221
		Cu- 9.77353	6.80112	10.60264
		Cu- 11.27406	6.81528	8.52535
		Cu- 9.77904	6.75834	6.48574
		Cu- 6.97504	4.57310	8.55470
		Cu- 8.44732	4.59653	10.61031
		Cu- 10.87805	4.61667	7.24549
		Cu- 8.46063	4.58020	6.49656
		Cu- 9.10474	8.09851	8.54176
		Cu- 9.12570	3.25058	8.53647



(a) (b) (c) (d)

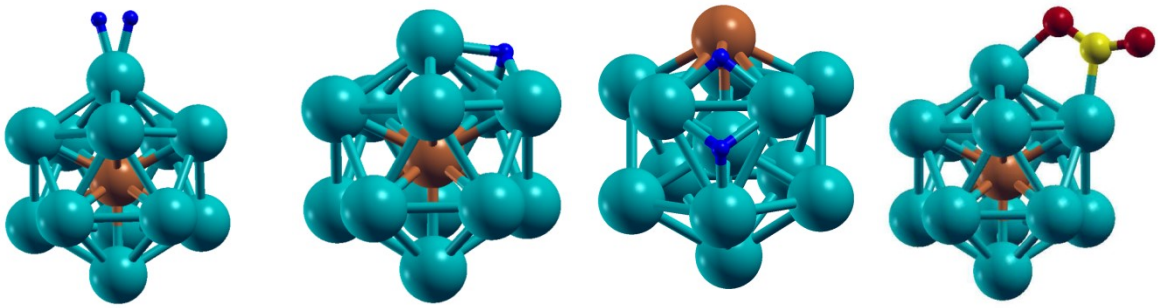


(e) (f) (g) (h)

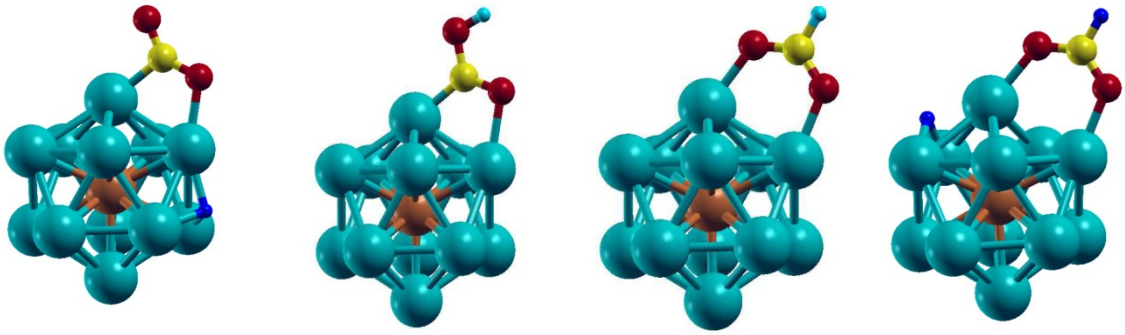


(i)

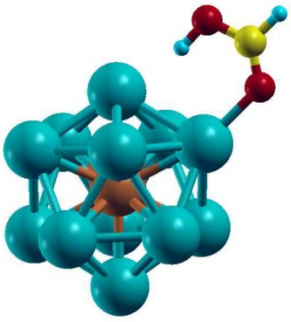
SF1: Lowest energy structure of Pd_4Cu_4 clusters along with their (a) H_2 (b) H (c) 2H (d) CO_2 (e) CO_2+H (f) Carboxyl (g) HCOO (h) HCOO+H and (i) HCOOH adsorbed species.



(a) (b) (c) (d)

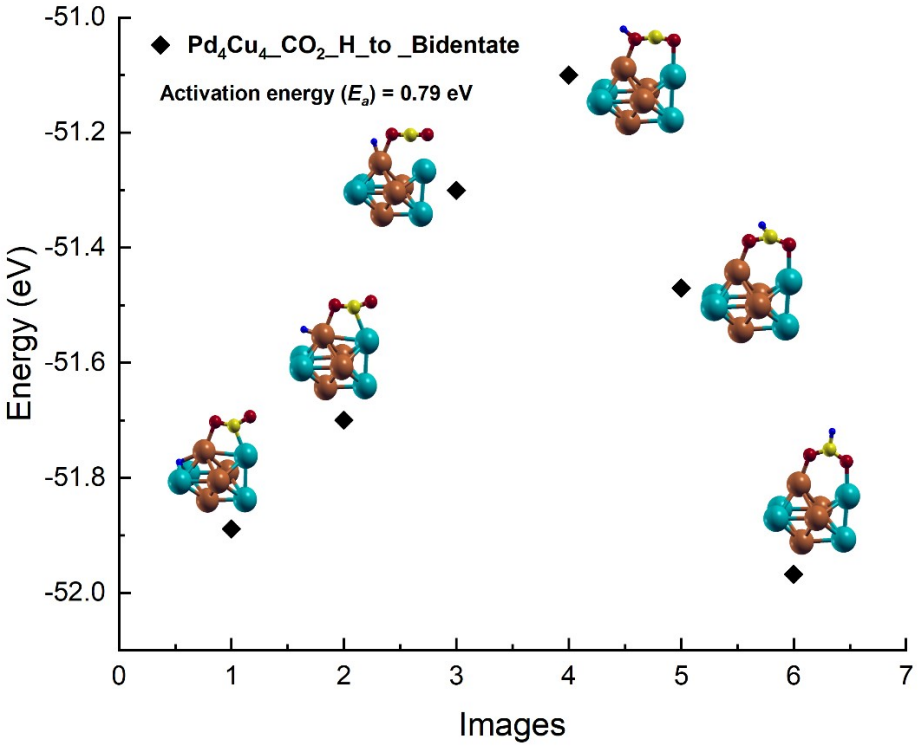


(e) (f) (g) (h)

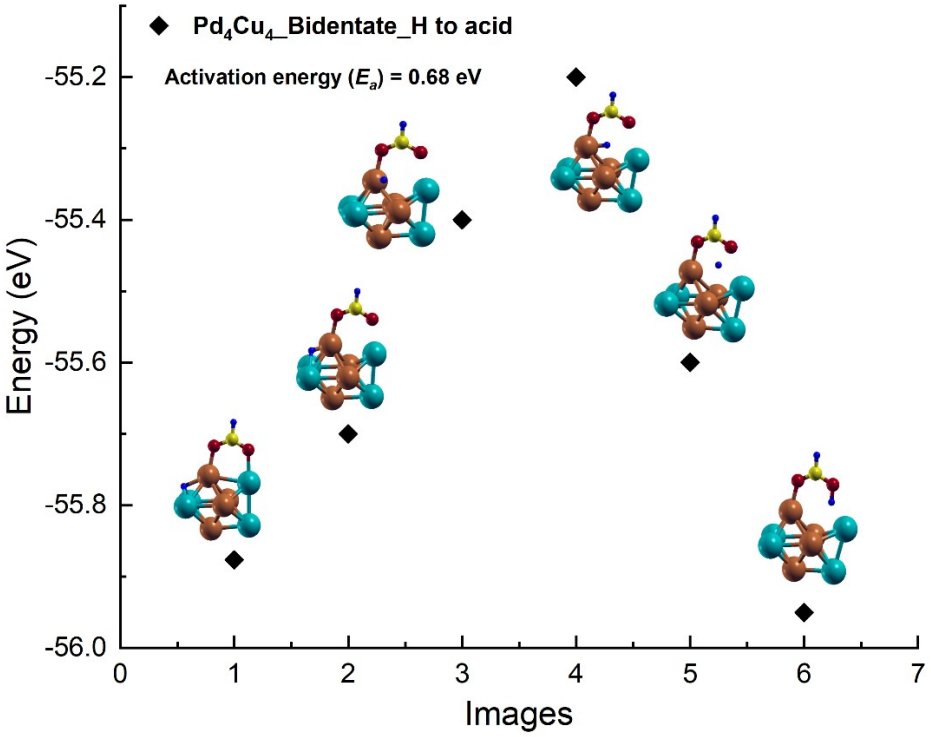


(i)

SF2: Lowest energy structure of $Pd_{12}Cu$ clusters along with their a) H_2 (b) H (c) 2H (d) CO_2 (e) CO_2+H (f) Carboxyl (g) HCOO (h) HCOO+H and (i) HCOOH adsorbed species.

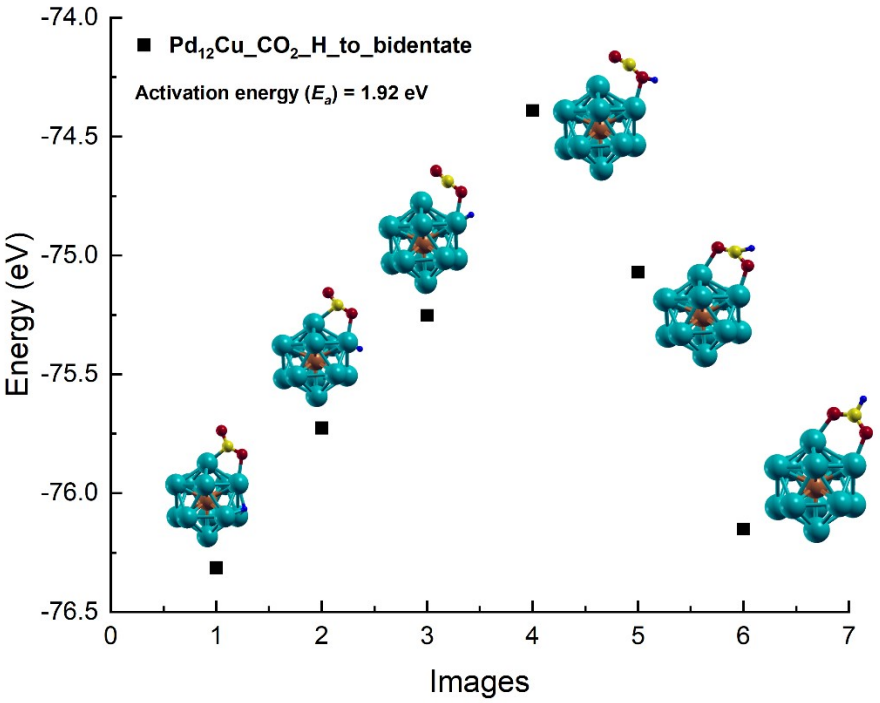


(a)

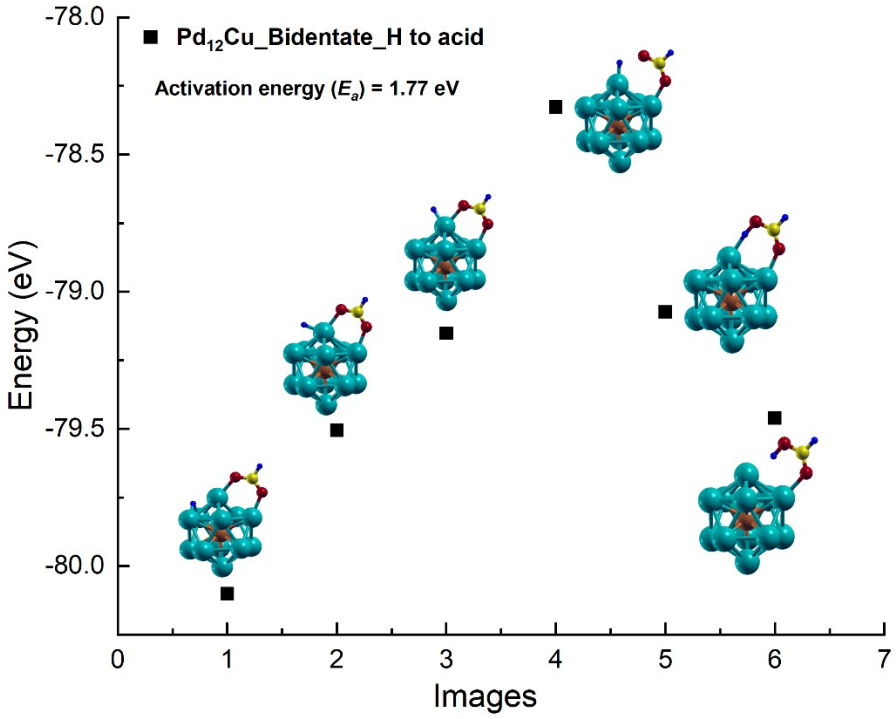


(b)

SF3: The potential energy profile for the formation of (a) bidentate formate by the reaction of H-atom and CO_2 (b) formic acid by the reaction of H-atom and formate on Pd_4Cu_4 cluster.

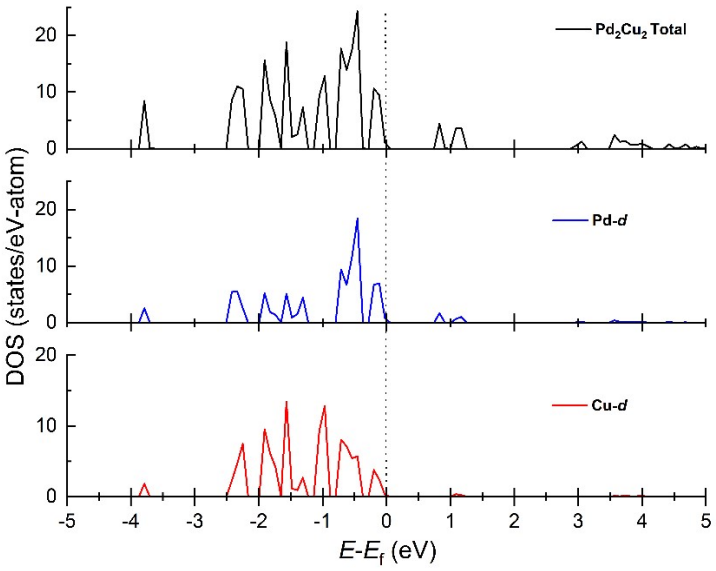


(a)

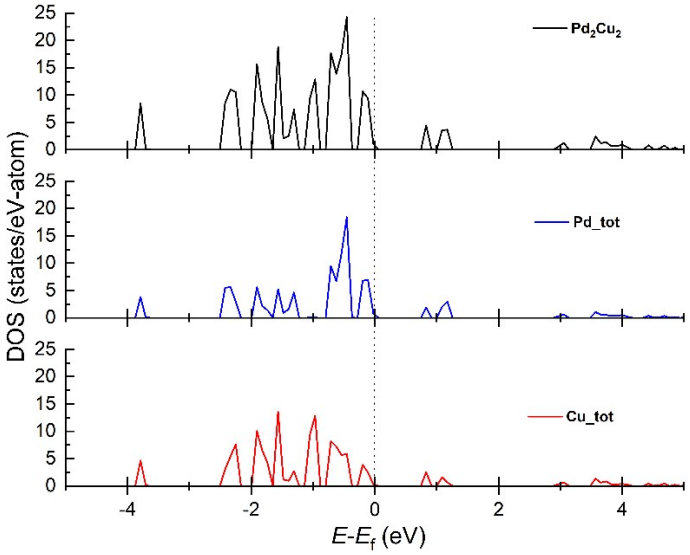


(b)

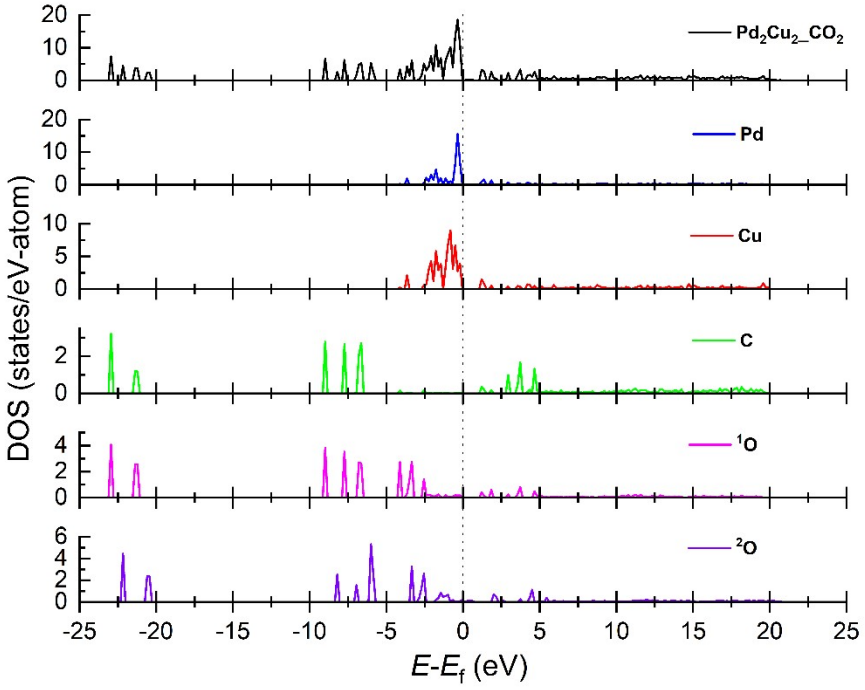
SF4: The potential energy profile for the formation of (a) bidentate formate by the reaction of H-atom and CO_2 (b) formic acid by the reaction of H-atom and formate on $Pd_{12}Cu$ cluster.



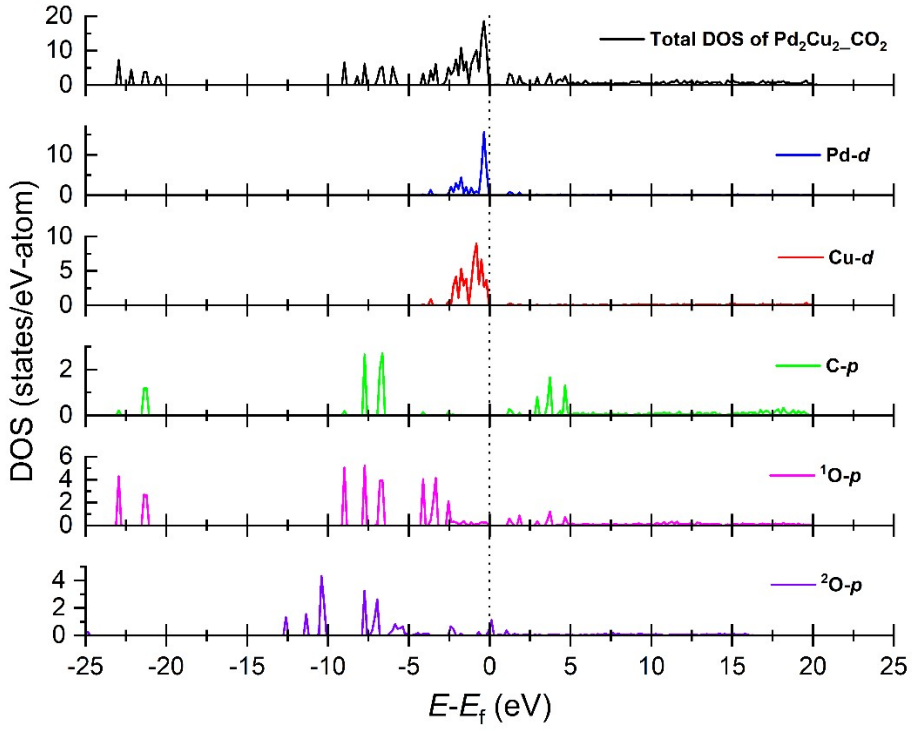
SF5(a): Total density of states of Pd_2Cu_2 cluster along with Pd and Cu in that cluster.



SF5(b): The orbital projected density of states of Pd_2Cu_2 cluster.



SF6(a): Total density of states of $Pd_2Cu_2_CO_2$cluster along with its constituent elements.



SF6(b): The orbital projected density of states of $Pd_2Cu_2_CO_2$cluster.