Electronic Supplementary Information:

Theoretical Study of Catalytic Oxidation of CO on free $Pd_XO_2^+$ (x = 4-6) Clusters: Size Dependent Comparison of Combustion

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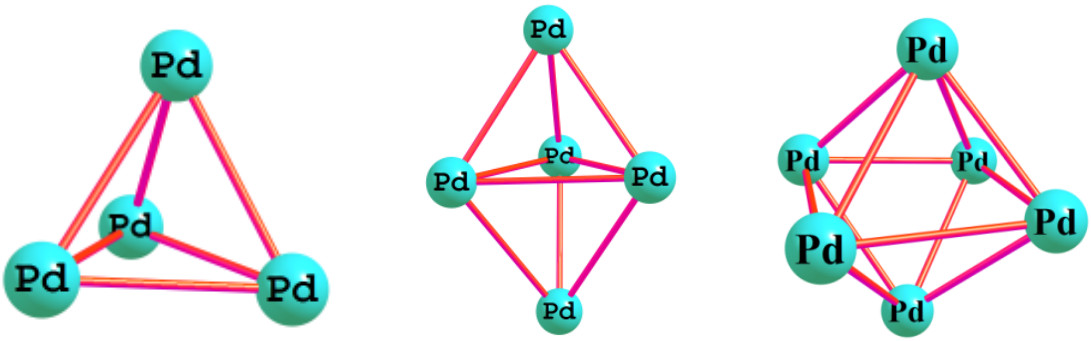
1. **Figure S1** Gas phase optimized geometries of the most stable conformer of Pd_4^+, Pd_5^+, and Pd_6^+ at M06-L/GENECP.



2. **Table S1** Relative Energies (ΔE, kcal/mol), enthalpies (ΔH, kcal/mol), and free energies (ΔG, kcal/mol) of all optimized stationary points involved in O_2 dissociation on Pd_4^+ cluster for generation of $Pd_4 2O^+$ in gas-phase, optimized at M06L/GENECP level of theory.

Species	ΔE	ΔH	ΔG
R1 (O_2+ Pd_4^+)	0.00	0.00	0.00
IM1	-41.33	-41.33	-33.61
TS_{1-2}	-32.50	-32.93	-23.99
IM2	-64.57	-65.02	-55.89
TS_{2-3}	-61.95	-62.64	-52.94
IM3	-62.62	-62.71	-54.26
TS_{3-4}	-62.16	-62.87	-52.99
IM4	-67.20	-67.53	-58.54

3. **Table S2** Relative Energies (ΔE, kcal/mol), enthalpies (ΔH, kcal/mol), and free energies (ΔG, kcal/mol) of all optimized stationary points involved in O_2 dissociation on Pd_5^+ cluster for generation of $Pd_5 2O^+$ in gas-phase, optimized at M06L/GENECP level of theory.

Species	ΔE	ΔH	ΔG
R2 (O_2+ Pd_5^+)	0.00	0.00	0.00
IM5	-42.53	-42.72	-33.51
TS_{5-6}	-41.34	-41.95	-31.31
IM6	-49.41	-49.85	-39.91
TS_{6-7}	-46.81	-47.51	-37.22
IM7	-67.34	-67.69	-58.39

4. **Table S3** Relative Energies (ΔE, kcal/mol), enthalpies (ΔH, kcal/mol), and free energies (ΔG, kcal/mol) of all optimized stationary points involved in O_2 dissociation on Pd_6^+ cluster for generation of Pd_62O^+ in gas-phase, optimized at M06L/GENECP level of theory.

Species	ΔE	ΔH	ΔG
R3 (O_2+ Pd_6^+)	0.00	0.00	0.00
IM8	-59.93	-60.55	-49.46
TS_{8-9}	-20.01	-20.73	-9.54
IM9	-67.28	-67.82	-57.41

5. **Table S4** Relative Energies (ΔE, kcal/mol), enthalpies (ΔH, kcal/mol), and free energies (ΔG, kcal/mol) of all optimized stationary points involved in the combustion reaction of CO in gas-phase on Pd_42O^+ cluster, optimized at M06L/GENECP level of theory.

Species	ΔE	ΔH	ΔG
IM4 + 2CO	0.00	0.00	0.00
IM10	-22.15	-22.53	-12.71
TS_{10-11}	-6.30	-7.11	3.67

IM11	-78.33	-78.71	-70.21
IM12	-65.60	-66.23	-65.93
IM13	-89.88	-90.66	-81.14
TS_{13-14}	-69.45	-70.58	-59.94
IM14	-134.20	-135.02	-126.98
P1 ($2CO_2$+ Pd_4^+)	-125.55	-126.96	-124.28

6. Table S5 Relative Energies (ΔE, kcal/mol), enthalpies (ΔH, kcal/mol), and free energies (ΔG, kcal/mol) of all optimized stationary points involved in the combustion reaction of CO in gas-phase on $Pd_5 2O^+$ cluster, optimized at M06L/GENECP level of theory.

Species	ΔE	ΔH	ΔG
IM7+ 2CO	0.00	0.00	0.00
IM15	-21.50	-22.01	-11.12
TS_{15-16}	-8.19	-9.15	3.03
IM16	-76.12	-76.55	-67.39
IM17	-64.31	-64.95	-63.96
IM18	-108.04	-109.19	-97.36
TS_{18-19}	-99.05	-100.64	-87.56
IM19	-100.24	-101.38	-89.45
TS_{19-20}	-80.97	-82.48	-69.53
IM20	-130.63	-131.44	-123.45
P2 ($2CO_2$+ Pd_5^+)	-125.41	-126.80	-124.43

7. Table S6 Relative Energies (ΔE, kcal/mol), enthalpies (ΔH, kcal/mol), and free energies (ΔG, kcal/mol) of all optimized stationary points involved in the combustion reaction of CO in gas-phase on $Pd_6 2O^+$ cluster, optimized at M06L/GENECP level of theory.

Species	ΔE	ΔH	ΔG
IM9 + 2CO	0.00	0.00	0.00
IM21	-25.86	-26.13	-16.58
TS_{21-22}	-4.10	-4.86	6.33
IM22	-70.21	-70.42	-62.20
IM23	-59.65	-60.28	-59.31
IM24	-98.09	-99.16	-88.46
TS_{24-25}	-55.60	-56.79	-45.53
IM25	-132.25	-133.10	-123.40
P3 ($2CO_2$+ Pd_6^+)	-125.46	-126.66	-125.41

8. Cartesian coordinates of all geometries, optimized at M06L/GENECP level of theory.

IM1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	1.684871	0.211952	-0.815681
2	46	0	-1.848939	-0.020779	-0.580103
3	46	0	-0.084877	1.493449	0.715512
4	8	0	-0.424967	-1.695440	-0.775591
5	8	0	0.109350	-0.833150	-1.699327
6	46	0	0.303835	-1.244867	1.110693

TS_{1-2}

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	46	0	1.159893	1.428597	-0.297303
2	46	0	-1.992828	-0.001636	-0.440035
3	46	0	-0.221005	-0.004542	1.533686
4	8	0	-0.323842	-0.899407	-1.419236
5	8	0	-0.327243	0.901491	-1.417234
6	46	0	1.167172	-1.422782	-0.303049

IM2

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	1.036647	1.376706	-0.639947
2	46	0	-2.062672	-0.004818	-0.478603
3	46	0	0.234430	0.003784	1.678597
4	8	0	-0.725586	-1.320038	0.214418
5	8	0	-0.731300	1.317247	0.213849
6	46	0	1.044967	-1.375187	-0.634528

TS_{2-3}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	1.240328	1.361988	-0.265764
2	46	0	-1.601905	0.001192	-1.037054
3	46	0	-0.633815	-0.002364	1.545838
4	8	0	-0.706563	-1.483414	0.071776
5	8	0	-0.707384	1.481979	0.076355
6	46	0	1.241296	-1.360567	-0.268782

IM3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	1.218183	1.307924	-0.268718
2	46	0	0.451171	-0.944995	1.315317
3	46	0	-0.197906	-1.044313	-1.305686
4	8	0	-1.479393	-1.013802	0.249685
5	8	0	1.685935	-0.615067	-0.243380
6	46	0	-1.507368	0.964666	0.257991

TS_{3-4}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-1.331716	1.200976	0.128225
2	46	0	-0.265699	-1.091315	-1.240160
3	46	0	0.182000	-0.862621	1.423432
4	8	0	1.547968	-0.924424	-0.064158
5	8	0	-1.801389	-0.673036	-0.066650
6	46	0	1.459488	1.030778	-0.288748

IM4

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.126616	0.082989	0.020842
2	46	0	-0.112425	0.042935	2.741416
3	46	0	2.448367	-0.256271	1.800500
4	8	0	1.400104	-1.319403	3.149707
5	8	0	-1.047604	0.956686	1.334069
6	46	0	0.631648	-2.330199	1.587342

IM5

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.521488	-1.846568	-0.381198
2	46	0	-0.043126	-0.189083	1.631010
3	46	0	1.943040	0.494365	-0.189164
4	46	0	-1.952740	-0.418864	-0.282456
5	46	0	-0.470521	1.900471	-0.172964
6	8	0	-0.333457	-0.424088	-1.799168
7	8	0	0.344145	0.767246	-1.680897

TS_{5-6}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-1.168417	1.609598	-0.274385
2	46	0	0.001089	-0.000065	1.646845

3	46	0	-1.657393	-1.121496	-0.271708
4	46	0	1.656802	1.121568	-0.272675
5	46	0	1.168211	-1.609557	-0.275125
6	8	0	0.152619	0.824362	-1.589886
7	8	0	-0.154297	-0.824634	-1.589590

IM6

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-1.633133	1.340629	-0.272086
2	46	0	0.000067	-0.000268	1.524958
3	46	0	-1.635047	-1.338826	-0.272037
4	46	0	1.634969	1.338972	-0.271908
5	46	0	1.633152	-1.340503	-0.272292
6	8	0	0.000989	1.274811	-1.255264
7	8	0	-0.001034	-1.274841	-1.255388

TS_{6-7}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-0.105992	1.874236	-0.258108
2	46	0	-0.120618	-0.113077	1.650384
3	46	0	-2.110471	-0.020721	-0.305848
4	46	0	2.091242	0.025872	-0.144704
5	46	0	0.159725	-1.859618	-0.421853
6	8	0	1.314034	1.241744	-1.427427
7	8	0	-0.818871	-0.705232	-1.561830

IM7

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	46	0	0.033924	0.757929	0.018096
2	46	0	0.054306	0.210502	2.785943
3	46	0	2.198981	-0.448614	1.297143
4	46	0	-1.999184	1.672984	1.603868
5	46	0	0.844813	2.618069	1.884994
6	8	0	-1.870765	0.661452	-0.050493
7	8	0	1.866017	1.408193	0.631431

IM8

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-0.253268	-1.929684	-0.062223
2	46	0	1.088633	-0.012526	1.354692
3	46	0	-1.604486	-0.010636	1.276627
4	8	0	3.241626	-0.001655	-0.421587
5	8	0	3.132653	-0.012712	0.848121
6	46	0	1.321882	0.010347	-1.231733
7	46	0	-0.247730	1.931153	-0.028937
8	46	0	-1.413601	0.013845	-1.382607

TS_{8-9}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.465503	-0.582188	1.646100
2	46	0	1.620230	1.208101	-0.323390
3	46	0	-0.970655	1.565351	0.745442
4	8	0	2.424757	-0.853755	-0.515710
5	8	0	2.276090	-0.103771	1.167556
6	46	0	0.642469	-1.671611	-0.751625
7	46	0	-0.699122	0.548614	-1.667984
8	46	0	-1.875964	-0.901740	0.238093

IM9

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	46	0	-1.537908	1.421813	0.080115
2	46	0	0.001787	0.000420	-1.726867
3	46	0	-1.538707	-1.421823	0.078585
4	8	0	1.963517	0.000408	-1.321373
5	8	0	-1.960292	0.000755	-1.322597
6	46	0	1.537980	1.420171	0.082610
7	46	0	1.539318	-1.419613	0.081940
8	46	0	-0.003031	-0.001170	1.863438

IM10

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.004056	-0.006719	-0.003442
2	46	0	-0.009190	0.000517	2.664972
3	46	0	2.553703	-0.019293	1.453555
4	8	0	1.749691	-0.959779	3.076314
5	8	0	-0.973899	1.006379	1.336109
6	46	0	1.114190	-2.335070	1.692163
7	6	0	-0.852750	0.658445	-1.678845
8	8	0	-1.388625	1.111198	-2.575106

$TS_{10\text{-}11}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.151576	0.194844	0.016887
2	46	0	0.102922	0.044336	2.850260
3	46	0	2.641348	-0.153724	1.565943
4	8	0	1.607119	-1.351785	2.814538
5	8	0	-1.226709	0.618308	1.391481
6	46	0	0.795142	-2.256855	1.201765
7	6	0	-1.214142	1.584100	-0.216383
8	8	0	-1.974881	2.395123	-0.495105

IM11

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	46	0	0.377438	-0.507629	-0.195826
2	46	0	0.006448	-0.077230	2.489870
3	46	0	2.621963	-0.120584	1.200433
4	8	0	1.710350	-1.014716	2.801162
5	8	0	-1.890310	1.116515	2.262078
6	46	0	1.184143	-2.449378	1.412911
7	6	0	-2.763515	1.817705	1.904247
8	8	0	-3.626187	2.506538	1.554835

IM12

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	1.463936	-0.788280	0.476330
2	46	0	-1.457960	-0.796864	0.479090
3	46	0	-0.002894	0.360885	-1.611184
4	8	0	0.004211	-1.497836	-0.703776
5	46	0	-0.003814	1.484752	0.778160

IM13

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.494308	-1.522334	-0.787421
2	46	0	-1.322414	-0.000705	0.688351
3	46	0	0.493776	1.523053	-0.786244
4	8	0	1.132470	0.001087	-1.776285
5	46	0	1.265865	-0.000288	1.292496
6	6	0	-3.114418	0.000204	-0.048931
7	8	0	-4.152982	0.000337	-0.528316

$TS_{13\text{-}14}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.036270	-1.591826	-0.712387
2	46	0	-0.877330	0.004093	1.357861
3	46	0	0.042307	1.590235	-0.715732
4	8	0	-0.917272	0.000669	-1.510999
5	46	0	1.844278	-0.002855	0.409710
6	6	0	-2.280860	0.001572	-0.060376

7	8	0	-3.383851	0.000190	-0.395564

IM14

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.671477	-0.889325	1.326600
2	46	0	-0.919571	0.708276	-0.013444
3	46	0	0.662697	-0.953429	-1.282622
4	8	0	-5.378176	-0.458529	-0.002633
5	46	0	1.660332	1.102021	-0.031184
6	6	0	-4.343567	0.062796	0.001378
7	8	0	-3.295027	0.598057	0.005339

IM15

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.179639	1.416848	-0.640409
2	46	0	-0.179339	-0.319658	1.637836
3	46	0	-2.246767	0.321042	-0.088250
4	46	0	2.089498	-0.777387	0.027199
5	46	0	-0.344036	-1.875446	-0.610777
6	8	0	2.064917	0.797834	-1.078798
7	8	0	-0.840900	-0.128450	-1.449999
8	6	0	0.757804	3.101917	0.125143
9	8	0	1.088414	4.103125	0.562749

$TS_{15\text{-}16}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.215052	1.202275	-0.789720
2	46	0	-0.090843	-0.230023	1.654508
3	46	0	-2.288838	0.615965	0.147525
4	46	0	1.985752	-0.924859	0.021624
5	46	0	-0.606349	-1.619931	-0.695224
6	8	0	2.243902	0.793338	-1.013482

7	8	0	-1.336899	0.086096	-1.513719
8	6	0	1.654139	2.229418	0.019094
9	8	0	2.367439	2.948792	0.565279

IM16

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-0.121594	-0.050726	0.217170
2	46	0	0.307570	0.195209	2.974331
3	46	0	2.520740	0.003045	1.338391
4	46	0	-1.578876	1.619503	1.812499
5	46	0	0.980687	2.439991	1.636543
6	8	0	-1.893271	-1.455245	0.204534
7	8	0	1.409607	1.175077	0.106172
8	6	0	-2.739720	-2.104148	-0.292668
9	8	0	-3.583914	-2.744744	-0.759622

IM17

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-2.252431	-0.004067	0.209209
2	46	0	0.038552	-1.437866	-0.792959
3	46	0	0.045281	1.467589	-0.742729
4	46	0	0.134404	-0.026300	1.570569
5	46	0	2.233057	-0.004712	0.013396
6	8	0	-1.143461	0.030792	-1.480548

IM18

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-2.336850	-0.443364	-0.101914
2	46	0	-0.358332	1.688209	-0.360001
3	46	0	0.054522	-0.376170	1.531620
4	46	0	0.185825	-0.924341	-1.324858

5	46	0	2.204454	0.483814	-0.048934
6	8	0	-1.564583	0.934031	1.103765
7	6	0	1.439391	-1.350097	0.190814
8	8	0	1.924728	-2.383311	0.501625

$TS_{18\text{-}19}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	2.360714	0.369325	-0.117258
2	46	0	0.362379	-1.515614	-0.654379
3	46	0	-0.065373	0.018830	1.516529
4	46	0	-0.242544	1.186122	-1.117680
5	46	0	-2.193340	-0.529404	-0.109938
6	8	0	1.863510	-0.492822	1.548201
7	6	0	-1.495868	1.283593	0.437148
8	8	0	-2.017164	2.236893	0.899610

IM19

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	2.338674	-0.126668	0.247184
2	46	0	0.247785	1.700769	-0.130429
3	46	0	0.060769	-0.797936	-1.232516
4	46	0	-0.275065	-0.422062	1.567693
5	46	0	-2.192239	0.423284	-0.295262
6	8	0	2.026318	-1.009078	-1.458267
7	6	0	-1.478106	-1.363465	0.262292
8	8	0	-1.952297	-2.438298	0.360692

$TS_{19\text{-}20}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-1.606227	1.233153	-0.429552
2	46	0	-0.423884	-0.134872	1.603322
3	46	0	-1.082186	-1.653976	-0.512954
4	46	0	1.116232	1.599485	0.116599
5	46	0	1.600479	-1.131133	0.097812
6	8	0	-0.612146	-0.028932	-1.612044
7	6	0	1.334368	0.259855	-1.364245
8	8	0	1.885986	0.336267	-2.397327

IM20

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-1.259134	-0.000121	0.632671
2	46	0	1.254195	0.000001	1.360519
3	46	0	0.237904	-1.928888	-0.271433
4	46	0	0.237675	1.928904	-0.271302
5	46	0	1.690887	0.000127	-1.218211
6	8	0	-3.593484	-0.000168	0.230329
7	6	0	-4.523045	-0.000065	-0.491825
8	8	0	-5.443011	0.000080	-1.196863

IM21

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-0.301320	1.544890	1.387643
2	46	0	1.622425	0.002602	-0.000554
3	46	0	-0.302192	1.544665	-1.387691
4	8	0	1.130757	-1.966463	-0.000468
5	8	0	1.132871	1.971947	-0.000549
6	46	0	-0.299223	-1.544378	1.391809
7	46	0	-0.300133	-1.544366	-1.391685
8	46	0	-2.101135	-0.003069	0.000657
9	6	0	3.579332	-0.002099	-0.000201
10	8	0	4.720943	-0.005881	0.000143

$TS_{21\text{-}22}$

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.812305	1.197304	1.323191
2	46	0	1.181882	-1.065538	-0.242799
3	46	0	0.540129	1.381753	-1.349815
4	8	0	-0.355913	-2.293880	-0.187416
5	8	0	2.371929	0.608583	-0.153856
6	46	0	-1.053501	-1.175925	1.416249
7	46	0	-1.327600	-0.966957	-1.372011
8	46	0	-1.662025	1.257121	0.261696
9	6	0	3.158118	-1.016775	-0.003629
10	8	0	4.291054	-1.161726	0.134055

IM22

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-0.308555	-1.250988	1.321647
2	46	0	-1.420210	0.972514	-0.004892
3	46	0	-0.302096	-1.254021	-1.322188
4	8	0	0.122025	2.202136	-0.003798
5	8	0	-3.411433	-0.193213	-0.005598
6	46	0	1.093973	1.146543	1.410439
7	46	0	1.101559	1.142781	-1.409017
8	46	0	2.004585	-1.083509	0.005148
9	6	0	-4.587018	-0.109633	-0.000975
10	8	0	-5.743552	-0.048296	0.003590

IM23

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	1.079742	-1.195034	-1.117170
2	46	0	1.098371	1.560716	-0.457931
3	46	0	1.067389	-0.388873	1.594795
4	8	0	2.246338	-0.016881	0.013871

5	46	0	-1.198447	0.365606	-1.502553
6	46	0	-1.210319	1.126069	1.049099
7	46	0	-1.227404	-1.465549	0.431347

IM24

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	-1.172230	0.991773	1.420144
2	46	0	1.419845	1.241717	-0.019179
3	46	0	-1.182436	0.951450	-1.437798
4	8	0	-0.388675	2.135993	-0.029086
5	46	0	0.722505	-1.083083	1.344628
6	46	0	0.712718	-1.119104	-1.324115
7	46	0	-1.565028	-1.386278	0.022321
8	6	0	3.136024	0.403022	-0.007261
9	8	0	4.158254	-0.117989	0.000027

TS_{24-25}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	46	0	0.698631	0.238176	-1.765954
2	46	0	-1.543273	-0.699317	-0.523220
3	46	0	-0.492895	1.789849	0.115607
4	8	0	-2.405212	1.109909	-0.462228
5	46	0	0.966424	-1.807805	-0.108112
6	46	0	-0.032114	-0.290811	1.813497
7	46	0	2.037091	0.687648	0.443891
8	6	0	-3.383699	-0.396924	0.103223
9	8	0	-4.451735	-0.339219	0.524477

IM25

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

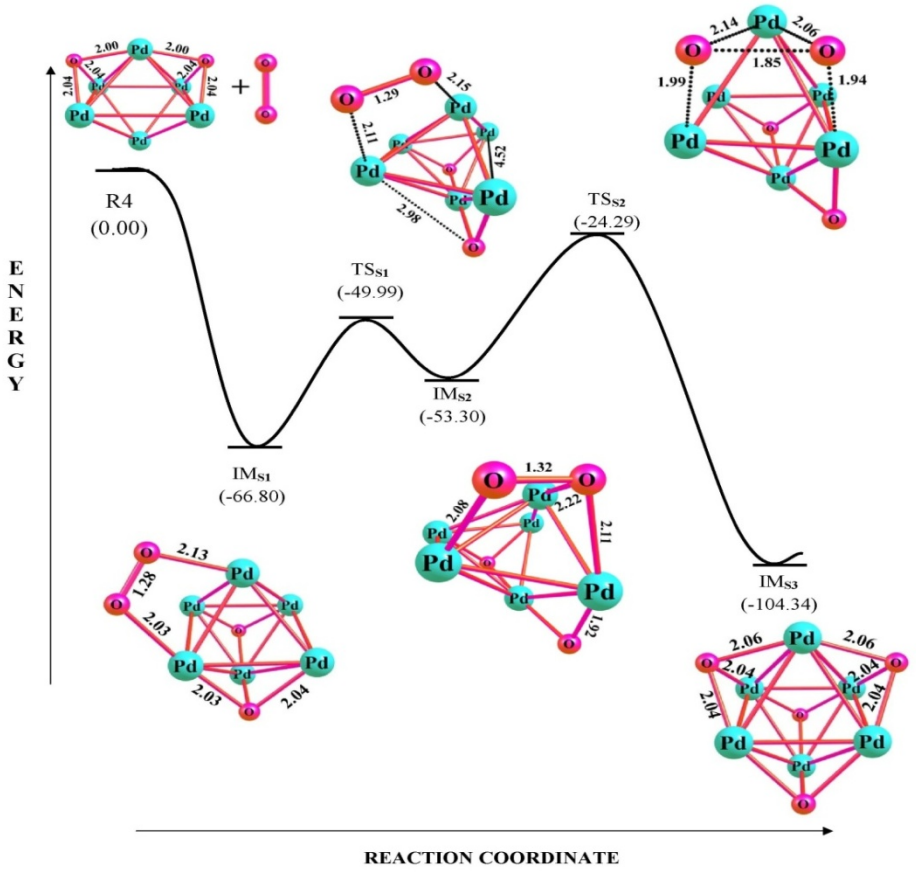
1	46	0	0.582599	0.097472	-1.890144
2	46	0	-1.028763	-1.335137	-0.265257
3	46	0	-1.025522	1.372174	-0.131520
4	8	0	-3.744441	1.152512	0.005881
5	46	0	1.615311	-1.351741	0.129993
6	46	0	0.009370	-0.095544	1.892715
7	46	0	1.621181	1.321850	0.271276
8	6	0	-3.717459	-0.018696	-0.014971
9	8	0	-3.668979	-1.190666	-0.035263

9. CO Oxidation Promoted by $Pd_6O_4^+$ clusters:

Similarly, like $Pd_6O_2^+$ system, $Pd_6O_4^+$ is formed by the straightforward association reaction:

$$Pd_6^+ + 2O_2 \rightarrow Pd_6O_2^+ + O_2 \rightarrow Pd_6O_4^+ \quad (1)$$

The PES depicted in Figure S2 represents the catalytic path of formation of $Pd_6O_4^+$ from



$Pd_6O_2^+$.

In the first step, O_2 is adsorbed on the bridge site to form IM_{S1}. Before dissociation of O_2, there is structural rearrangement in IM_{S1} resulting IM_{S2} via TS_{S1} with activation barrier of 16.81 Kcal mol^{-1}. Structural fluxionality of the cluster favors the dissociation of O_2 in the next step. IRC calculation of TS_{S2} signifies that the dissociation of O_2 leads to the formation of IM_{S3}, where all the O atoms are at the hollow site. The energy barrier for TS_{S2} is 29.01 Kcal mol^{-1}.

According to the previous experimental study the catalytic activity of $Pd_6O_4^+$ in CO oxidation in presence of oxygen is realized through the following stepwise reactions.

Figure S2. Potential energy profile (with ZPE corrected) for the dissociation of O_2 on $Pd_6O_2^+$ cluster in gas phase at M06-L/GENECP. All the energies are given in Kcal mol^{-1} in the parenthesis. All bond lengths and angels are in Å and (°) unit respectively.

$$Pd_6O_4^+ + CO \rightarrow Pd_6O_4CO^+ \quad (2)$$

$$Pd_6O_4CO^+ \rightarrow Pd_6O_3^+ + CO_2 \quad (3)$$

$$Pd_6O_3^+ + O_2 \rightarrow Pd_6O_5^+ \quad (4)$$

$$Pd_6O_5^+ + CO \rightarrow Pd_6O_5CO^+ \quad (5)$$

$$Pd_6O_5CO^+ \rightarrow Pd_6O_4^+ + CO_2 \quad (6)$$

The PES is depicted in Figure S3.

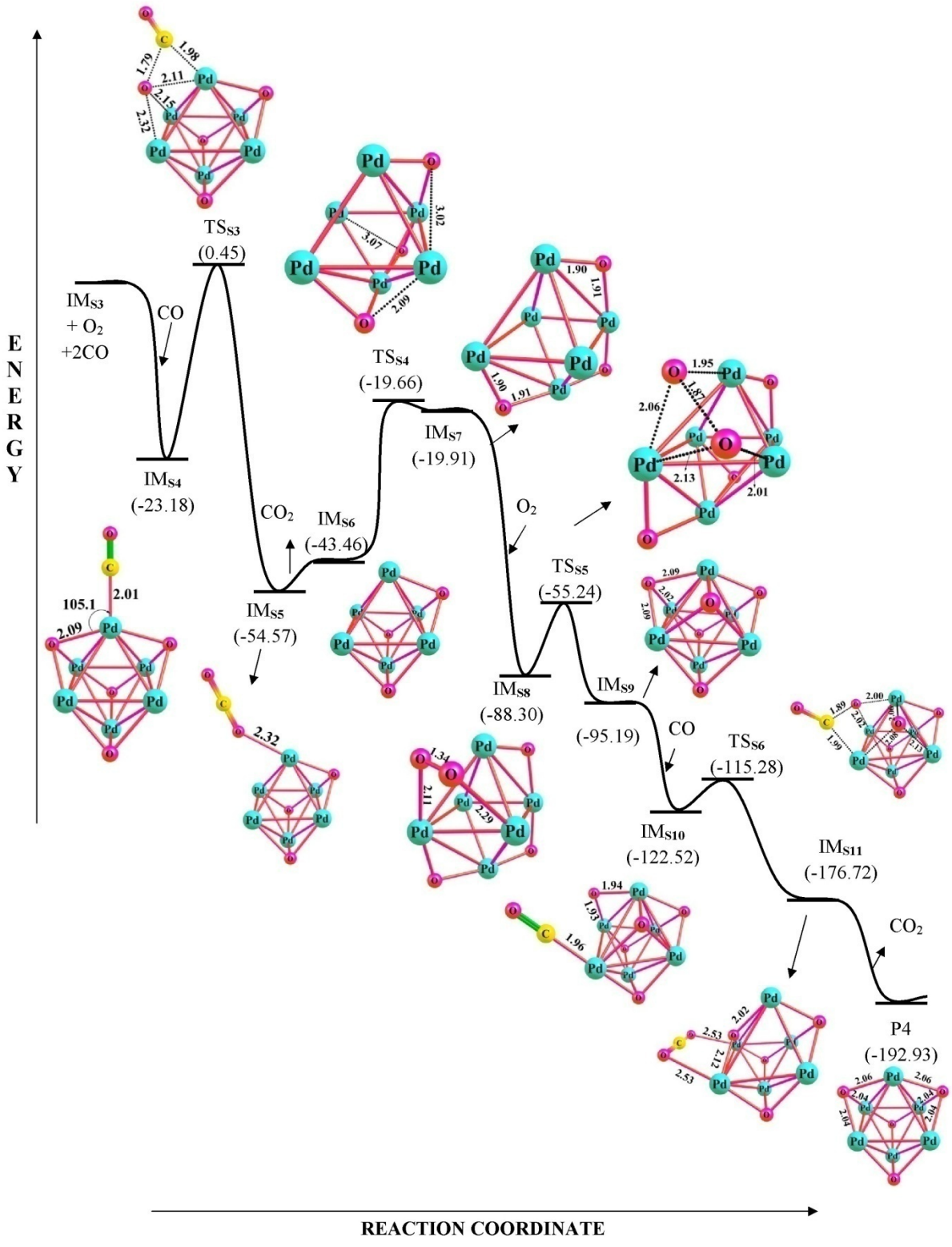


Figure S3. Potential energy profile (with ZPE corrected) for the oxidation of CO on oxide $Pd_6O_4^+$ cluster in gas phase at M06-L/GENECP. All the energies are given in Kcal mol^{-1} in the parenthesis. All bond lengths and angels are in Å and (°) unit respectively.

The first part of this mechanism passes through the barrier-free adsorption of CO at the top

position of the oxide cluster to form $Pd_6O_4CO^+$ (IM_{S4}, E_{ads} is 23.18 Kcal mol^{-1}). The adsorbed CO reacts with the dissociated oxygen atom of $Pd_6O_4^+$ to form CO_2 with activation barrier of 23.63 Kcal mol^{-1}, whereas previously reported[24] activation barrier for CO oxidation on $Pd_6O_4^+$ is 28.13 Kcal mol^{-1}. IRC calculation confirms that TS_{S3} is the perfect TS in between IM_{S4} and IM_{S5}. The elimination of the formed CO_2 molecule yields $Pd_6O_3^+$ (IM_{S6}). Before adsorption of O_2 on $Pd_6O_3^+$, the structural rearrangement occurs from IM_{S6} to IM_{S7} via TS_{S4} (activation barrier is 23.80 Kcal mol^{-1} which is higher than the previously reported[24] activation barrier of 17.52 Kcal mol^{-1}. The positions of all the three O atoms change from hollow site to bridge site in IM_{S7}. Another barrier less adsorption of O_2 on IM_{S7} forms IM_{S8}. This adsorbed O_2 molecule is activated by dissociation through TS_{S5} (barrier height 33.06 Kcal mol^{-1}) to form intermediate, IM_{S9}, as per equation (4), where all the dissociated O atoms are in the hollow site. In the next step, CO molecule is adsorbed on $Pd_6O_5^+$ to form $Pd_6O_5CO^+$ (IMS_{10}) intermediate with E_{ads} of 27.33 Kcal mol^{-1}. It is interesting to note that in IM_{S10} one dissociated oxygen atom changes its position from hollow to bridge site. This oxygen atom at bridge site causes combustion of the adsorbed CO via TS_{S6} (activation barrier 7.24 Kcal mol^{-1} and previously reported[24] activation barrier is 18.67 Kcal mol^{-1}) to form CO_2 intermediate product (IM_{S11}). This catalytic cycle is closed by reformation of $Pd_6O_4^+$ through desorption of CO_2.

Table S7 Average bond lengths (Å) of the most stable clusters as a function of cluster size

Average bond length (Å)		
Cluster size	Present Study	Previous Study[a]
4	2.61	2.64
5	2.66	2.69
6	2.68	2.71

[a] Taken from Ref: 83

Table S8 Theoretical and experimental results of bond length R (Å), binding energy BE (eV) for Pd-O system.

Species	R	BE
Pd-O	1.82 (1.79 [a])	2.63 (2.90[b])

Available theoretical and experimental values are given in the parenthesis.
[a] taken from Ref: 47
[b] taken from Ref: 73