Supporting Information

Density Functional Theory Study on Nucleation and Growth of Pt_n Clusters on γ-Al_2O_3(001) Surface

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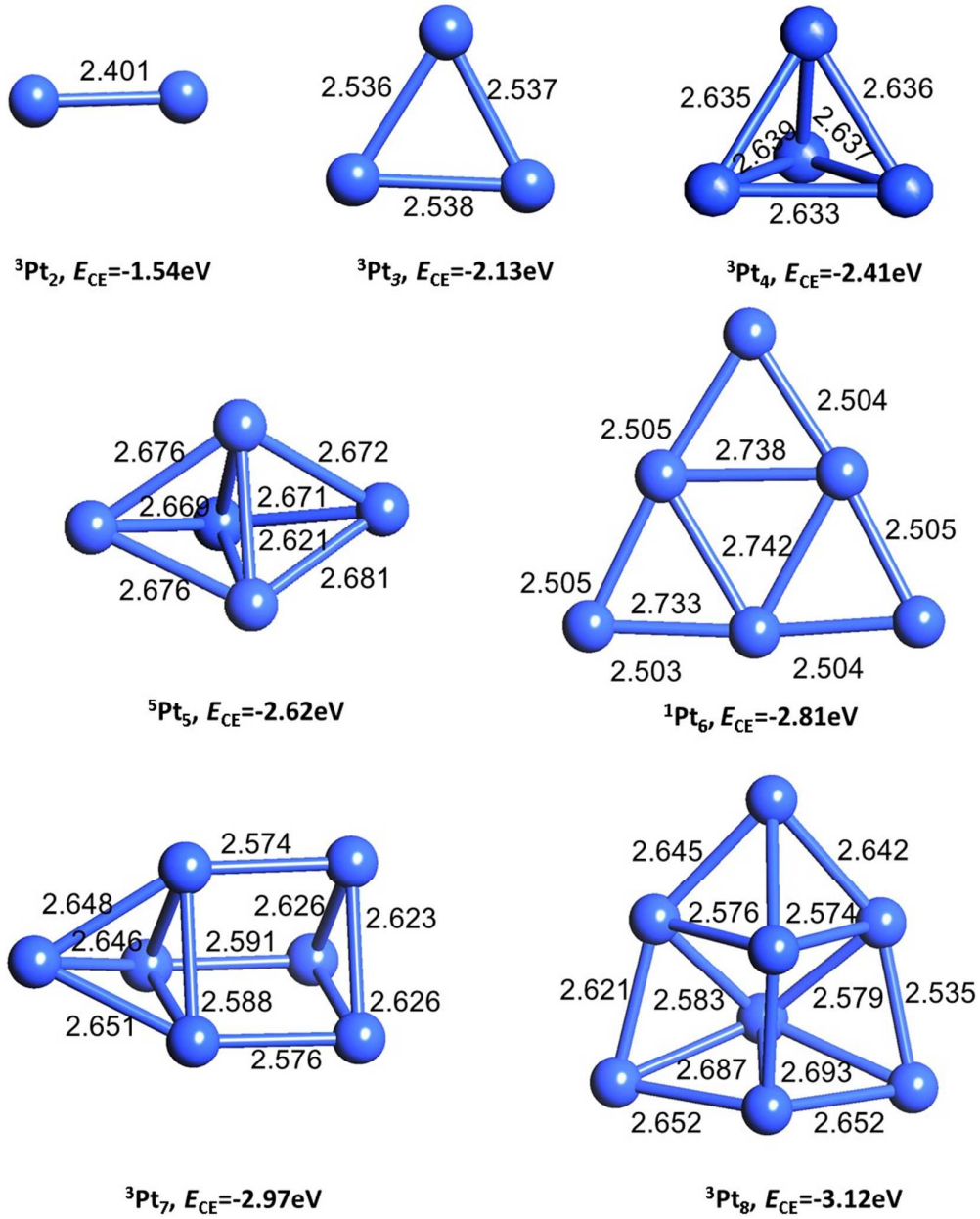
Table S1. Test on all atoms of the γ-Al_2O_3(001) support relaxed and the uppermost one layer of the γ-Al_2O_3(001) relaxed.

Configuration	Relax all（Total energy/Ha）	Relax one layer（Total energy/Ha）
γ-Al_2O_3(001)	-11376.29625	-11376.29625
Pt1-1	-11571.88927	-11571.88927

Table S2. The Relative energies (E_R, eV), Binding energies (E_{BE}, eV), γ-Al_2O_3(001) deformation energies ($\Delta E_{def,Al_2O_3}$, eV), clusters deformation energies ($\Delta E_{def,Pt_n}$, eV), metal-support interaction energies (E_{MS}, eV), metal-metal bond energy ($\Delta E_{bond,Pt_n}$, eV), bond length (Å) and electron transfer (ET, *e*) for corresponding configurations, $\bar{l}$ with a threshold of 3.0 Å.

Configuration	E_R	E_{BE}	$\Delta E_{def,Al_2O_3}$	$\Delta E_{def,Pt_n}$	E_{MS}	$\Delta E_{bond,Pt_n}$	Pt-Al $\bar{l}$	Pt-O $\bar{l}$	Pt-Pt $\bar{l}$	ET
Pt2-3	1.67	-1.93	0.64	0.04	-1.05	-1.51	2.616	2.215	2.567	0.121
Pt2-4	1.67	-1.94	0.58	0.44	-1.20	-1.32		2.059	2.688	0.106
Pt3-3	0.34	-2.86	0.56	0.00	1.28	-2.13		2.228	2.533	0.125
Pt3-4	0.43	-2.83	1.31	0.89	-2.30	-1.84		2.106	2.471	0.282
Pt3-5	0.45	-2.82	1.43	0.00	-1.12	-2.13		2.140	2.546	0.050
Pt3-6	1.10	-2.60	0.79	0.01	-1.27	-2.13	2.607	2.647	2.560	0.044
Pt4-3	0.77	-3.04	1.17	0.08	-1.85	-2.36	2.697	2.107	2.596	0.184
Pt4-4	0.86	-3.02	0.70	0.12	-1.34	-2.38		2.281	2.664	0.214
Pt4-5	1.02	-2.98	0.61	0.07	-1.19	-2.40	2.587	2.279	2.651	0.291
Pt4-6	1.04	-2.97	0.71	0.15	-1.30	-2.37		2.153	2.661	0.117
Pt4-7	1.14	-2.94	0.61	0.13	-1.18	-2.38		2.286	2.663	0.184
Pt4-8	1.21	-2.93	0.80	0.24	-1.38	-2.35	2.531	2.288	2.606	0.323
Pt5-3	0.75	-3.16	1.09	0.31	-1.68	-2.56	2.485	2.209	2.676	0.261
Pt5-4	0.83	-3.14	1.72	0.21	-2.29	-2.57	2.622	2.187	2.622	0.362
Pt5-5	0.88	-3.13	0.79	0.33	-1.37	-2.55		2.182	2.620	0.138
Pt5-6	1.11	-3.08	1.47	0.81	-2.10	-2.45	2.695	2.186	2.610	0.210
Pt5-7	1.16	-3.07	1.15	0.20	-1.65	-2.57	2.770	2.535	2.603	0.477
Pt5-8	1.18	-3.07	0.62	0.18	-1.11	-2.58	2.848	2.185	2.544	0.261
Pt6-3	0.22	-3.37	0.65	0.15	-1.25	-2.77		2.168	2.539	0.183
Pt6-4	0.24	-3.36	1.83	0.40	-2.45	-2.74	2.631	2.108	2.612	0.557
Pt6-5	0.25	-3.36	1.82	0.39	-2.44	-2.74	2.673	2.092	2.650	0.476
Pt6-6	0.67	-3.29	1.93	0.32	-2.51	-2.71	2.572	2.187	2.597	0.279
Pt7-3	0.14	-3.40	1.36	0.25	-1.90	-2.87		2.415	2.603	0.222
Pt7-4	0.24	-3.39	1.12	0.13	-1.55	-2.95	2.660	2.206	2.639	0.268
Pt7-5	0.43	-3.36	0.90	0.10	-1.31	-2.95		2.161	2.616	0.143
Pt7-6	0.62	-3.33	1.03	0.20	-1.42	-2.94		2.297	2.656	0.302
Pt7-7	1.16	-3.26	1.22	0.24	-1.67	-2.80	2.535	2.187	2.589	0.149
Pt7-8	1.37	-3.23	0.89	0.19	-1.30	-2.81	2.597	2.253	2.598	0.377
Pt8-3	1.23	-3.38	2.05	0.30	-2.45	-2.98	2.660	2.408	2.602	0.628
Pt8-4	2.21	-3.26	1.94	0.13	-2.23	-2.97	2.661	2.135	2.607	0.601



$^3Pt_2$, E_{CE}=-1.54eV $^3Pt_3$, E_{CE}=-2.13eV $^3Pt_4$, E_{CE}=-2.41eV

$^5Pt_5$, E_{CE}=-2.62eV $^1Pt_6$, E_{CE}=-2.81eV

$^3Pt_7$, E_{CE}=-2.97eV $^3Pt_8$, E_{CE}=-3.12eV

Figure S1. The most stable geometries, spin multiplicity and the cohesive energies of the Pt_n (n = 2–8) clusters in gas phase. The prefix superscript denotes the spin multiplicity.

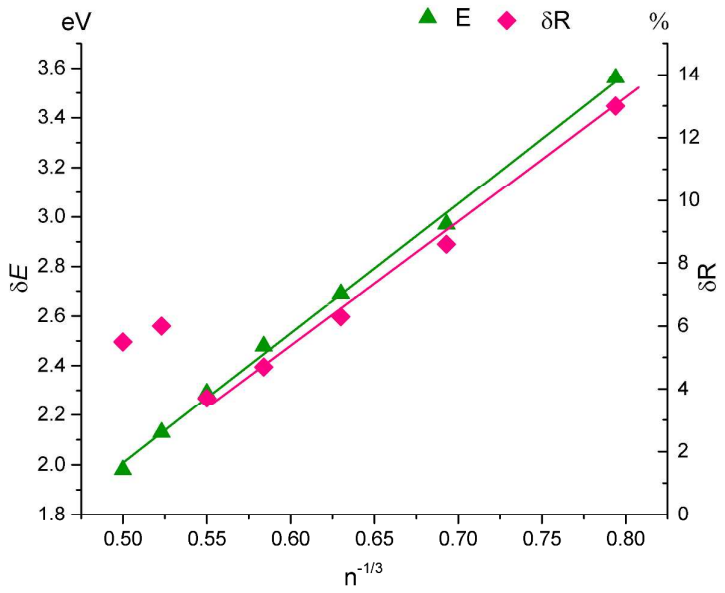


Figure S2. Difference between cluster cohesive energy and bulk cohesive energy E as a function of $n^{-1/3}$, difference between the average Pt–Pt bond distance in the cluster and the bond distance in the bulk as a function of $n^{-1/3}$, where n is the number of Pt atoms in the cluster.

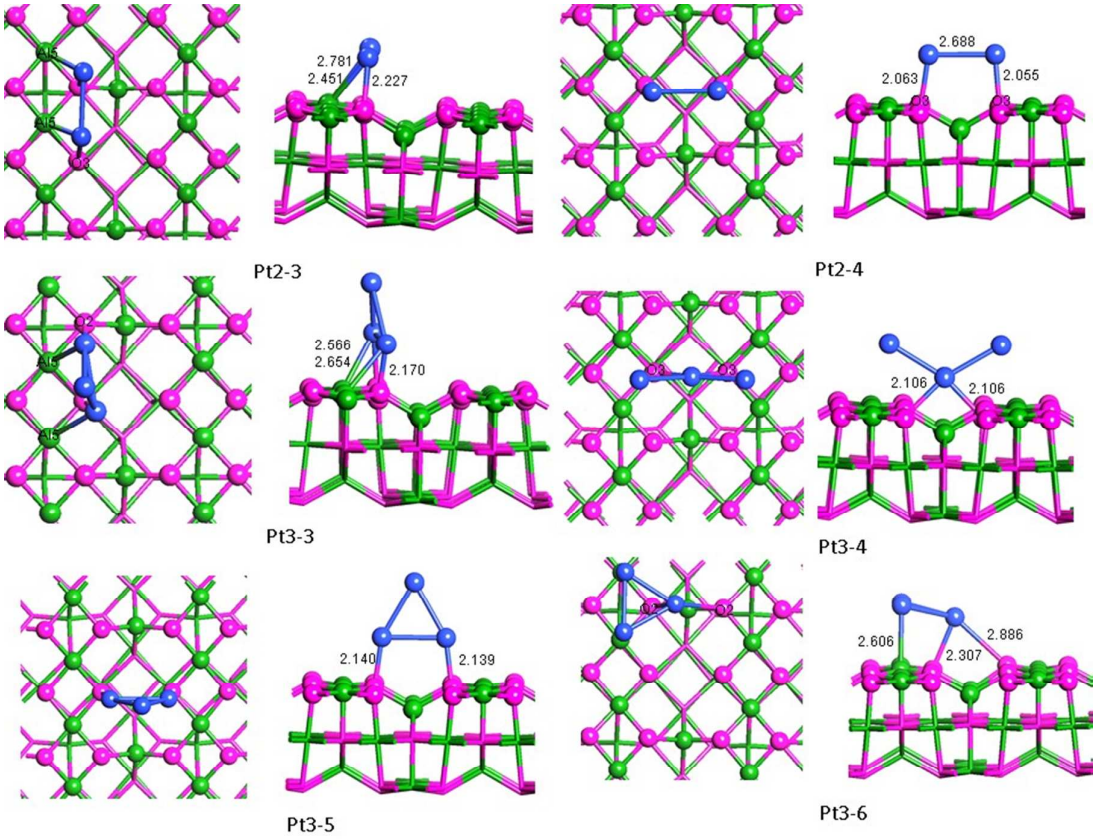


Figure S3. Top and side view for the remaining Pt_2 and Pt_3 adsorption configurations on γ-Al_2O_3(001) surface.

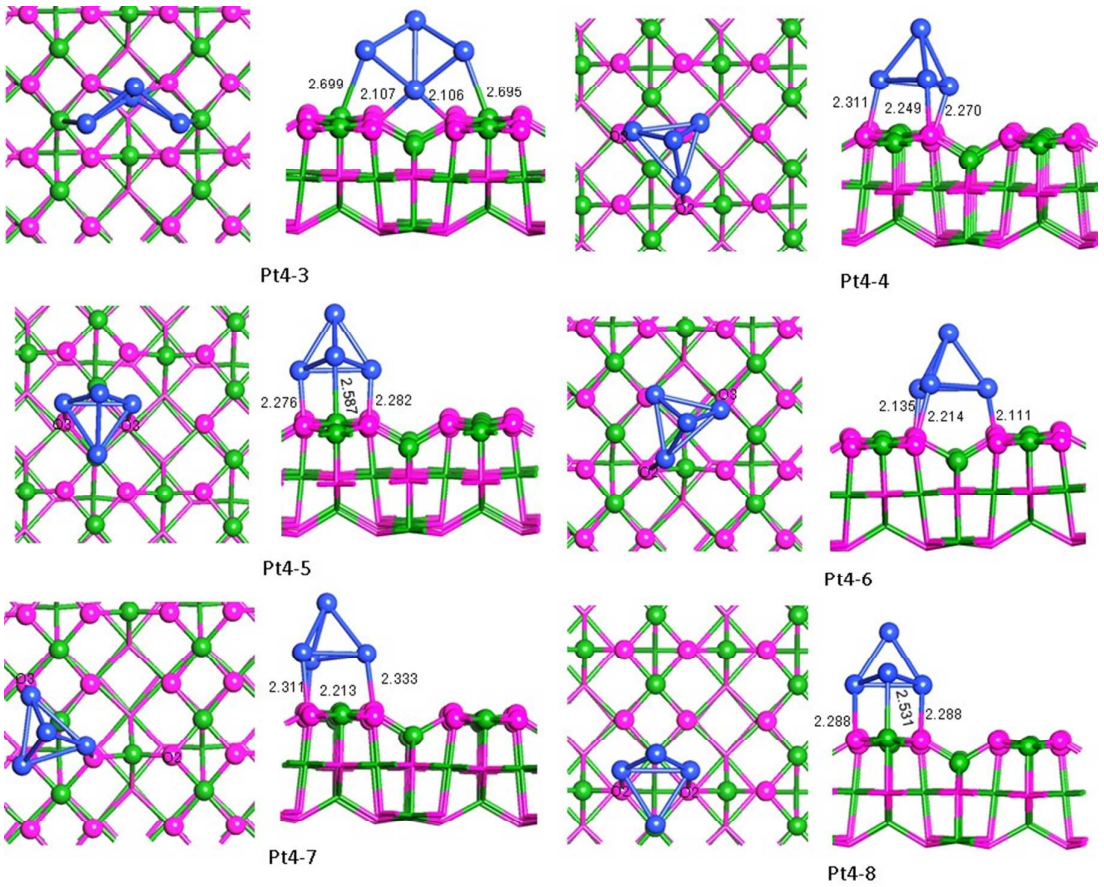


Figure S4. Top and side view for the remaining Pt_4 adsorption configurations on γ-Al_2O_3(001) surface.

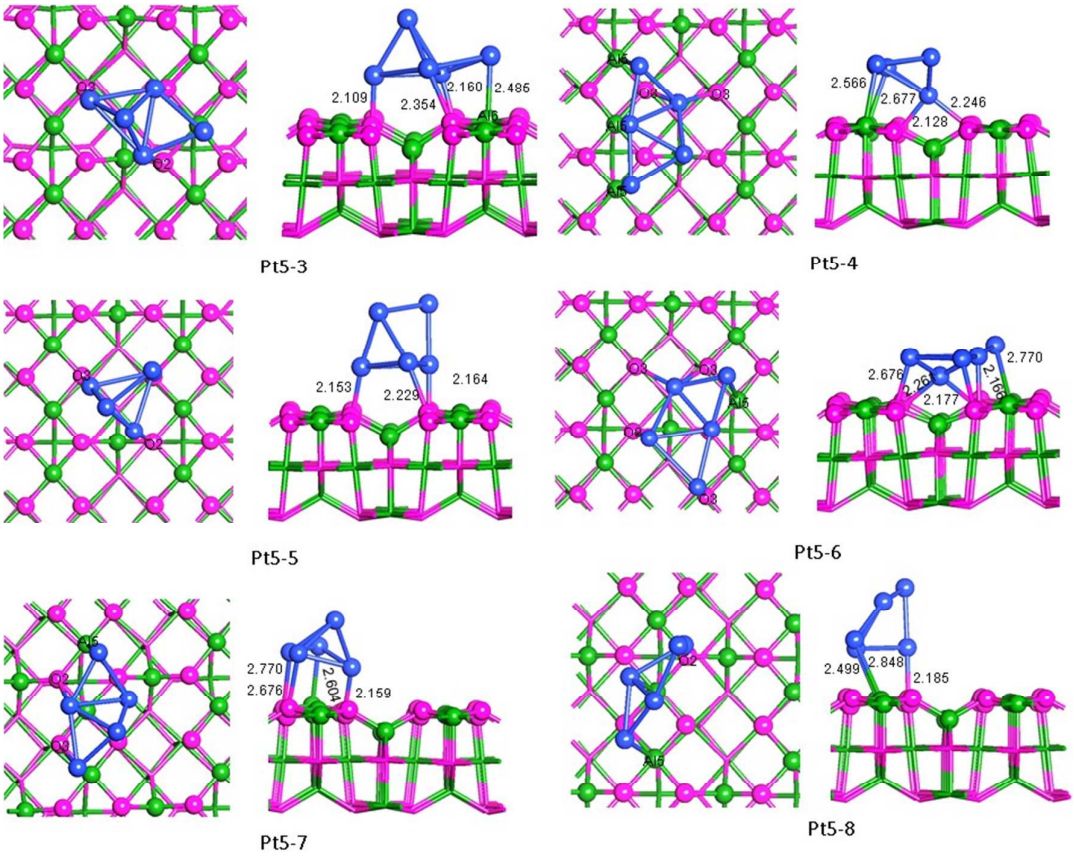


Figure S5. Top and side view for the remaining Pt_5 adsorption configurations on γ-Al_2O_3(001) surface.

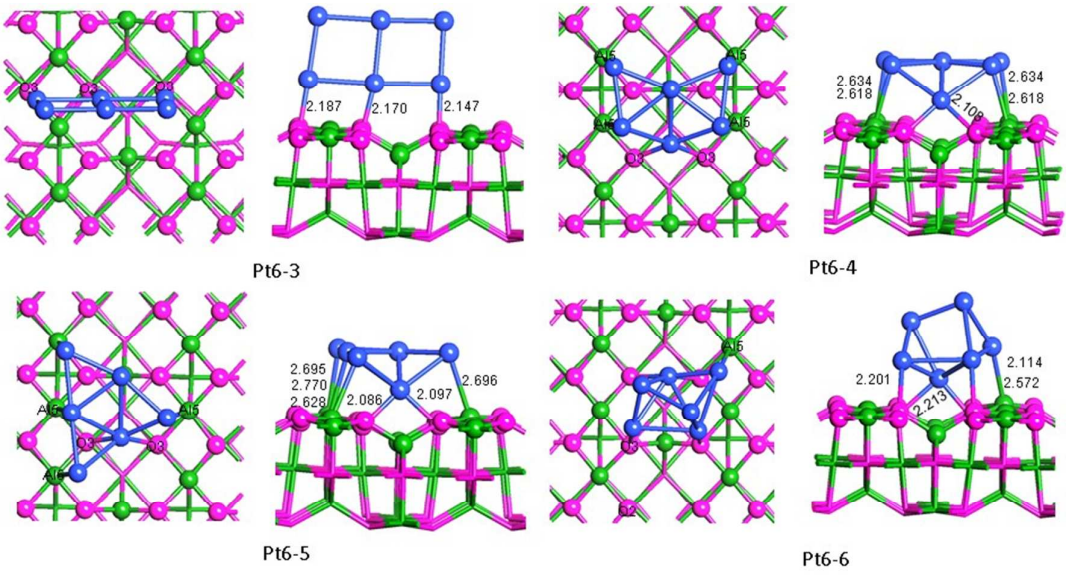


Figure S6. Top and side view for the remaining Pt_6 adsorption configurations on γ-Al_2O_3(001) surface.

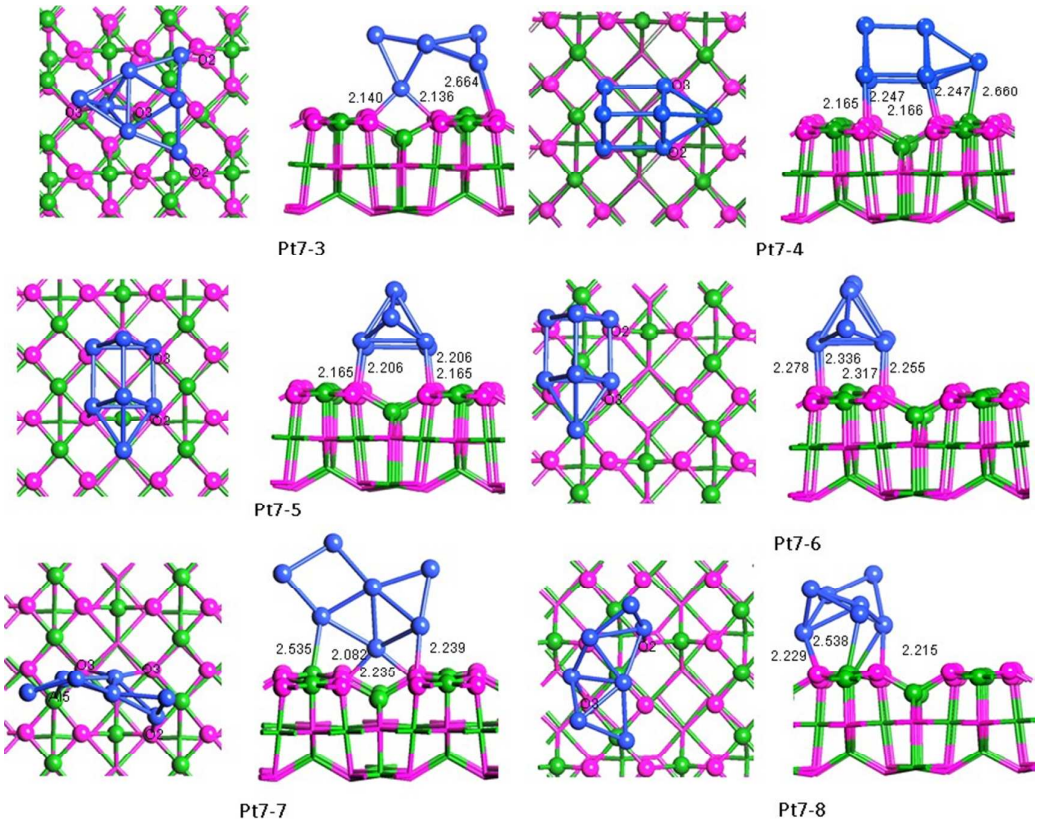


Figure S7. Top and side view for the remaining Pt_7 adsorption configurations on γ-Al_2O_3(001) surface.

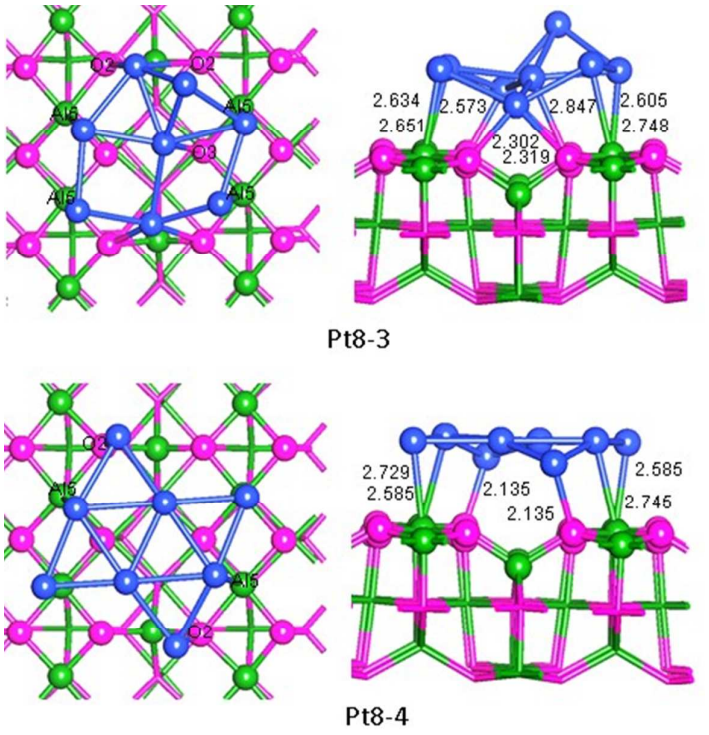


Figure S8. Top and side view for the remaining Pt_8 adsorption configurations on γ-Al_2O_3(001) surface.

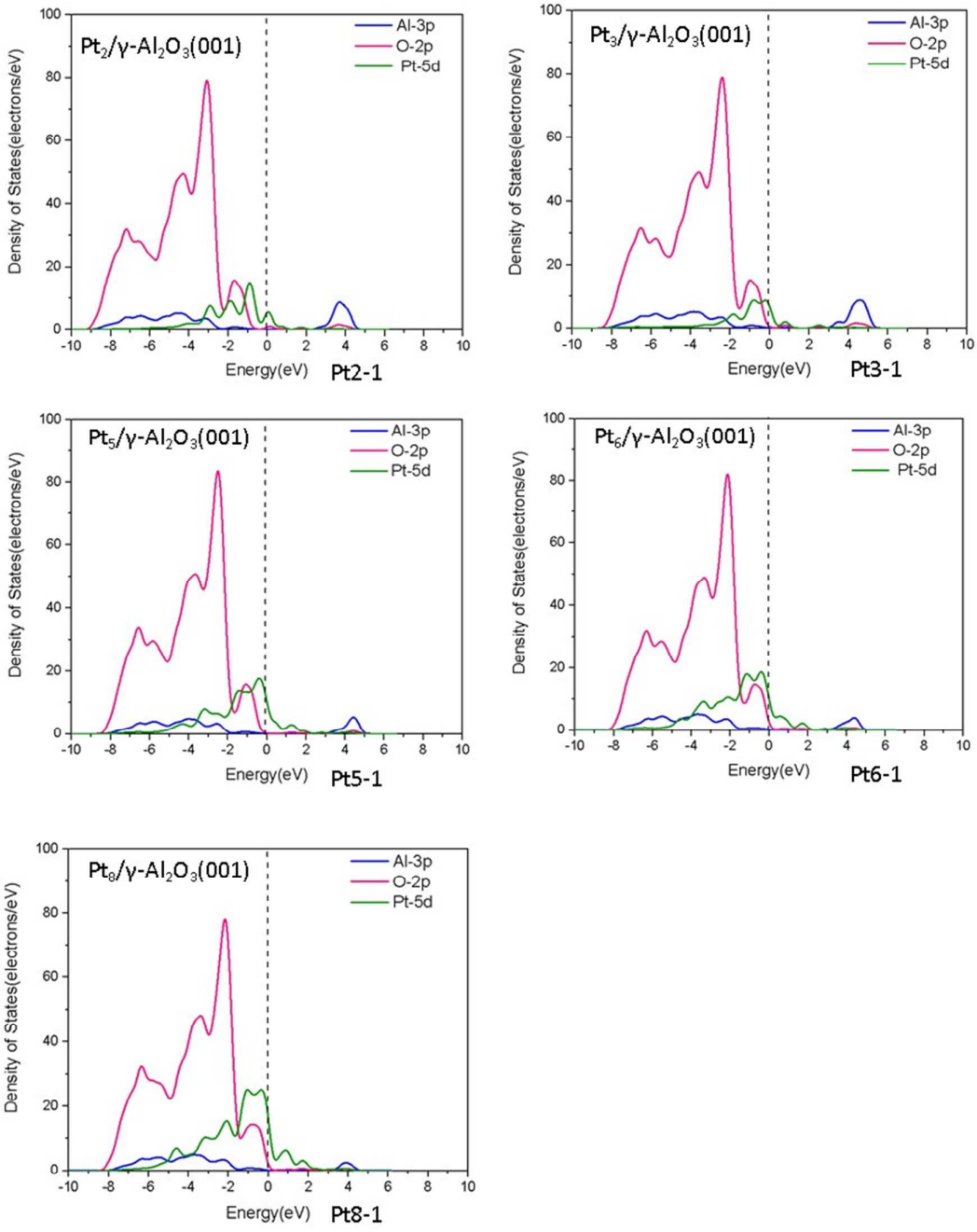


Figure S9. Density of states of Pt2-1, Pt3-1, Pt5-1, Pt6-1 and Pt8-1.

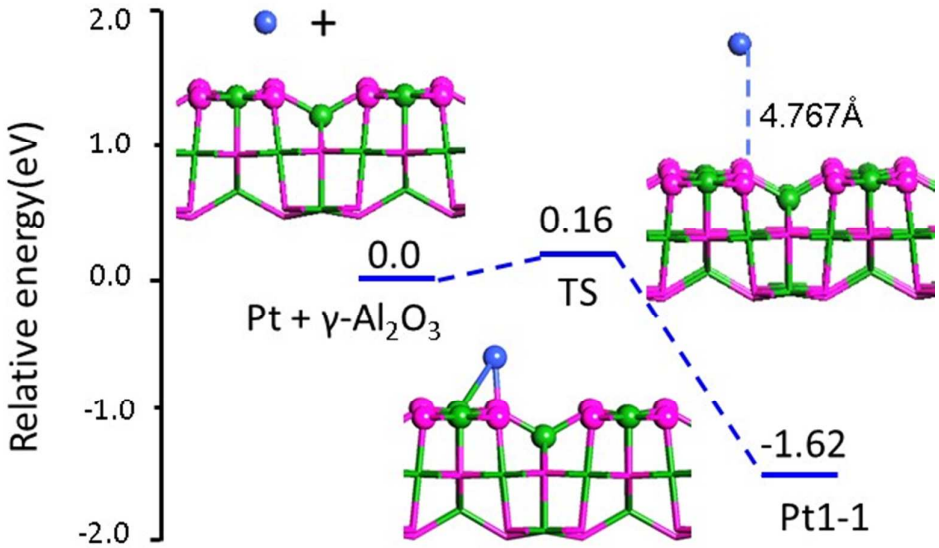


Figure S10. Diffusion barrier for Pt_1 on γ-Al_2O_3(001) surface.

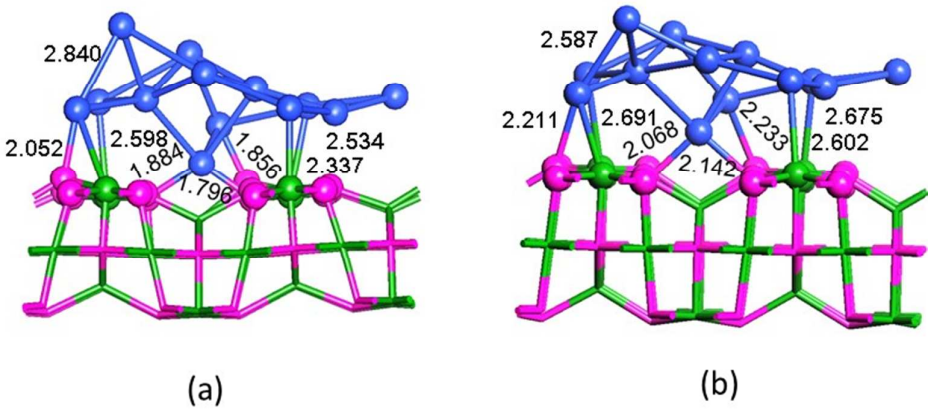


Figure S11. The Pt_{13} adsorption configuration on γ-Al_2O_3(001) surface, (a) using MD simulation with universal force field and (b) using GGA-PW91 functional with DNP basis set.

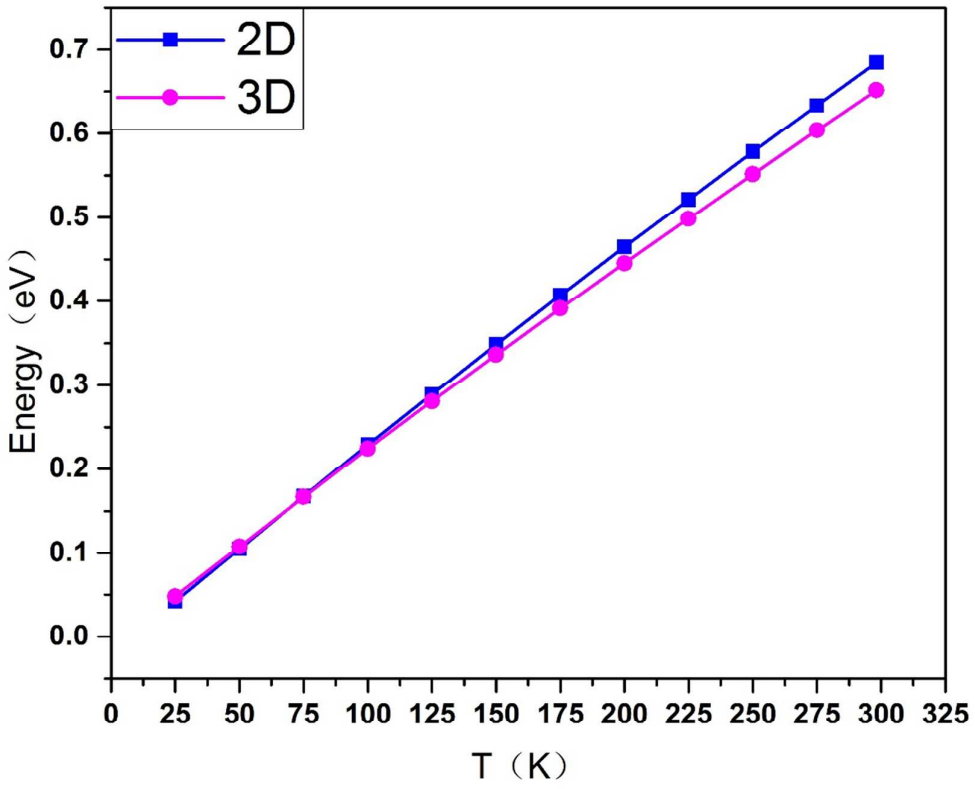


Figure S12. The relative energy of 3D-Pt_4 adsorption configuration relative to 2D-Pt_4 adsorption configuration on γ-Al_2O_3(001) surface as a function of temperature *T* (25 – 300K).