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

ORR viability of alumina supported platinum nanocluster: Exploring the oxidation behaviour by DFT methods

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Supporting Information

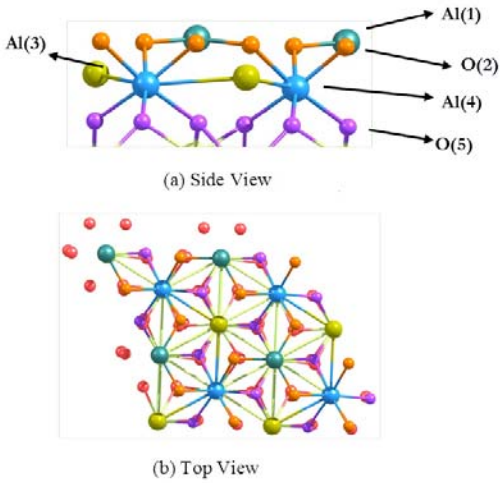

Figure-S1: Side and top view of α-Al_2O_3(0001) surface

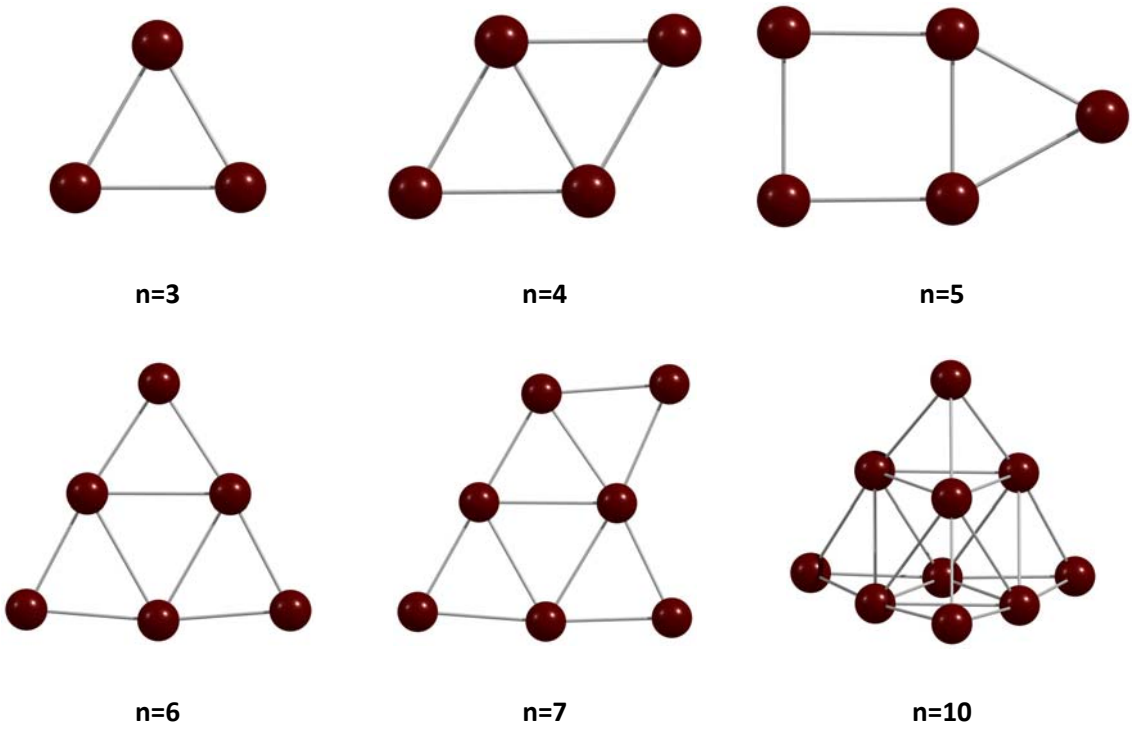

Figure-S2: Ground state structure of Pt_n clusters in the gas phase.

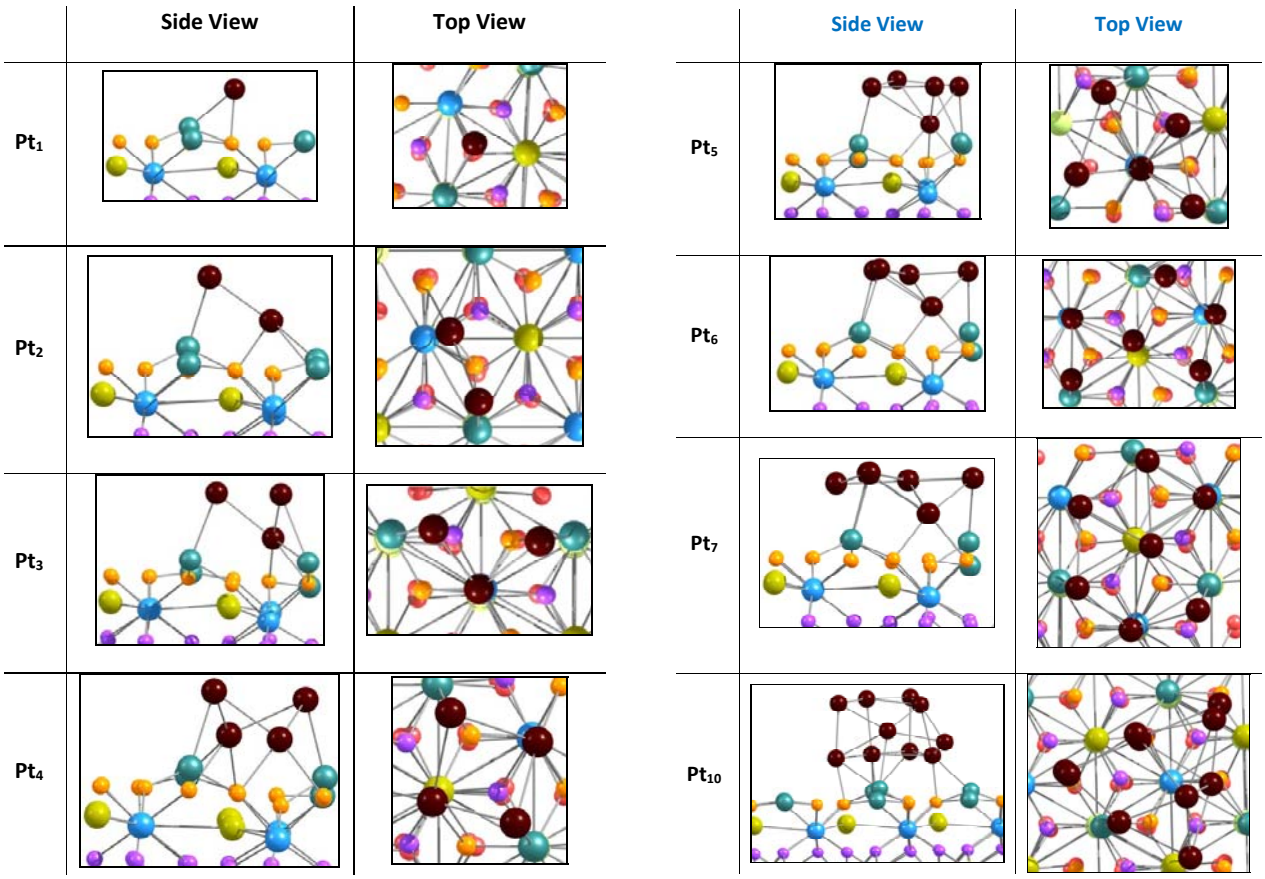

Figure-S3: Side and top view of ground state structure of alumina supported Pt_n clusters.

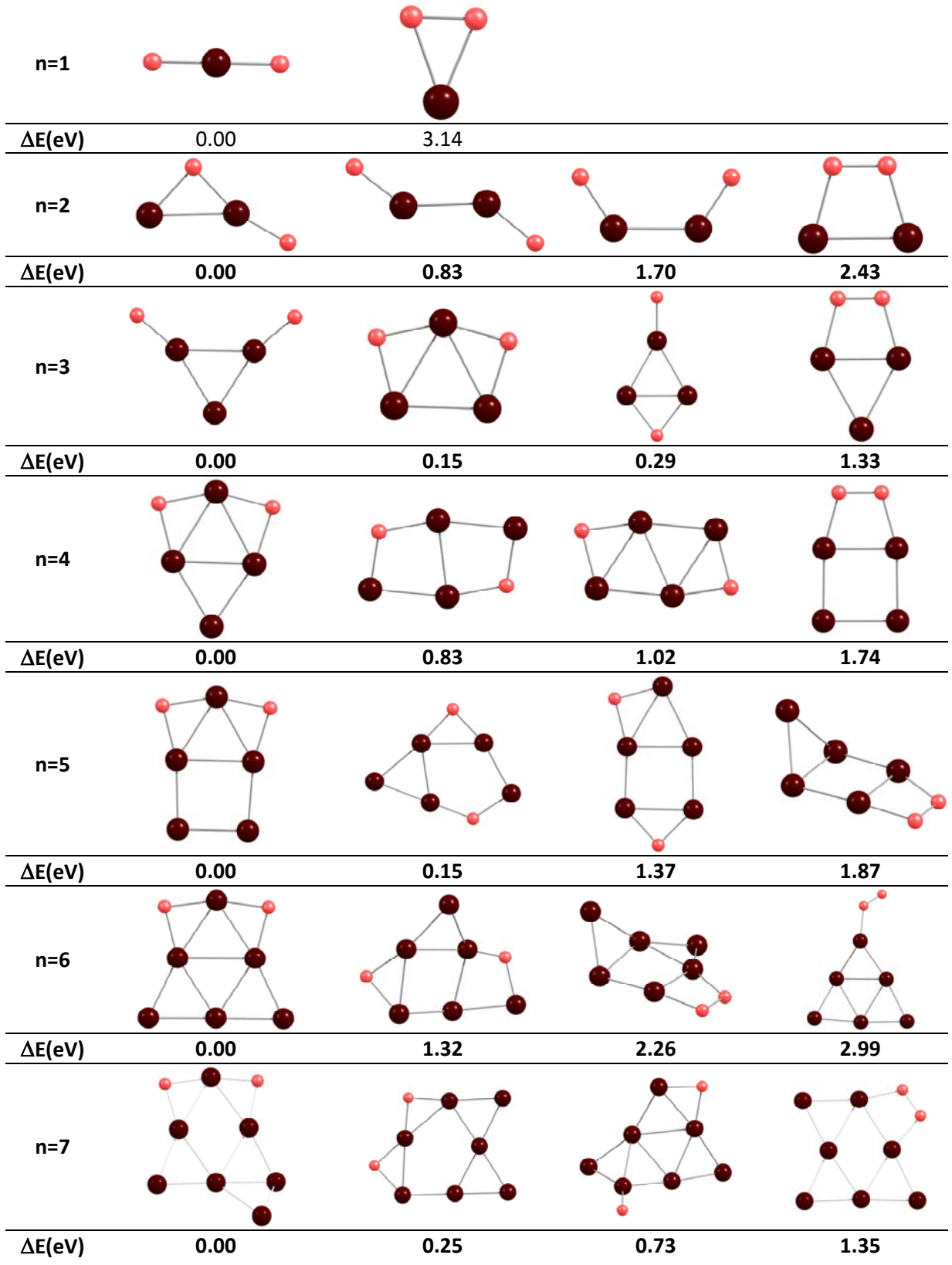

Figure S4: Low lying isomers of $Pt_n@O_2$. Relative stability (ΔE-eV) is also presented.

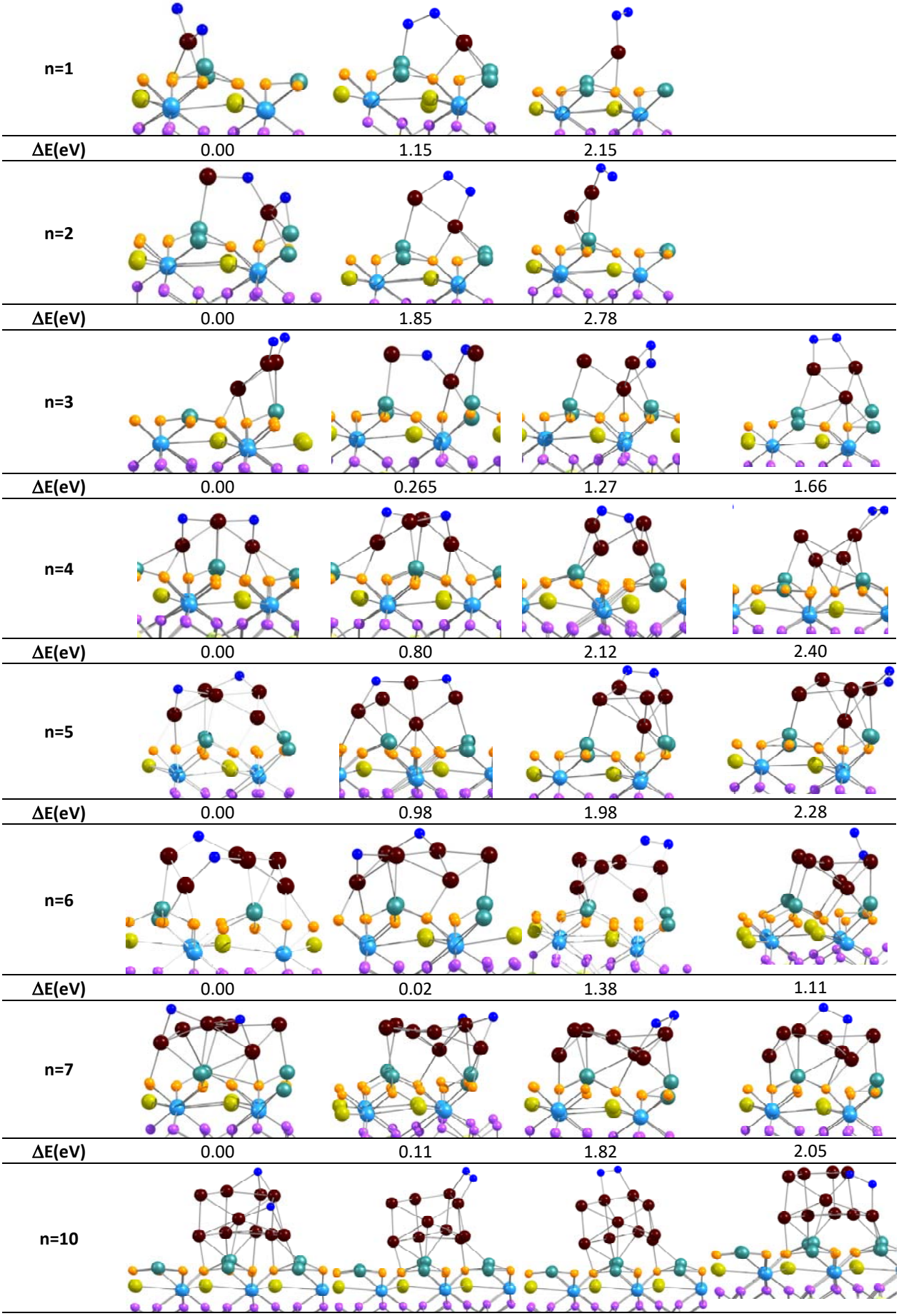

Figure S5: Low lying isomers of alumina supported-$Pt_n@O_2$. Relative stability (ΔE-eV) is also presented.

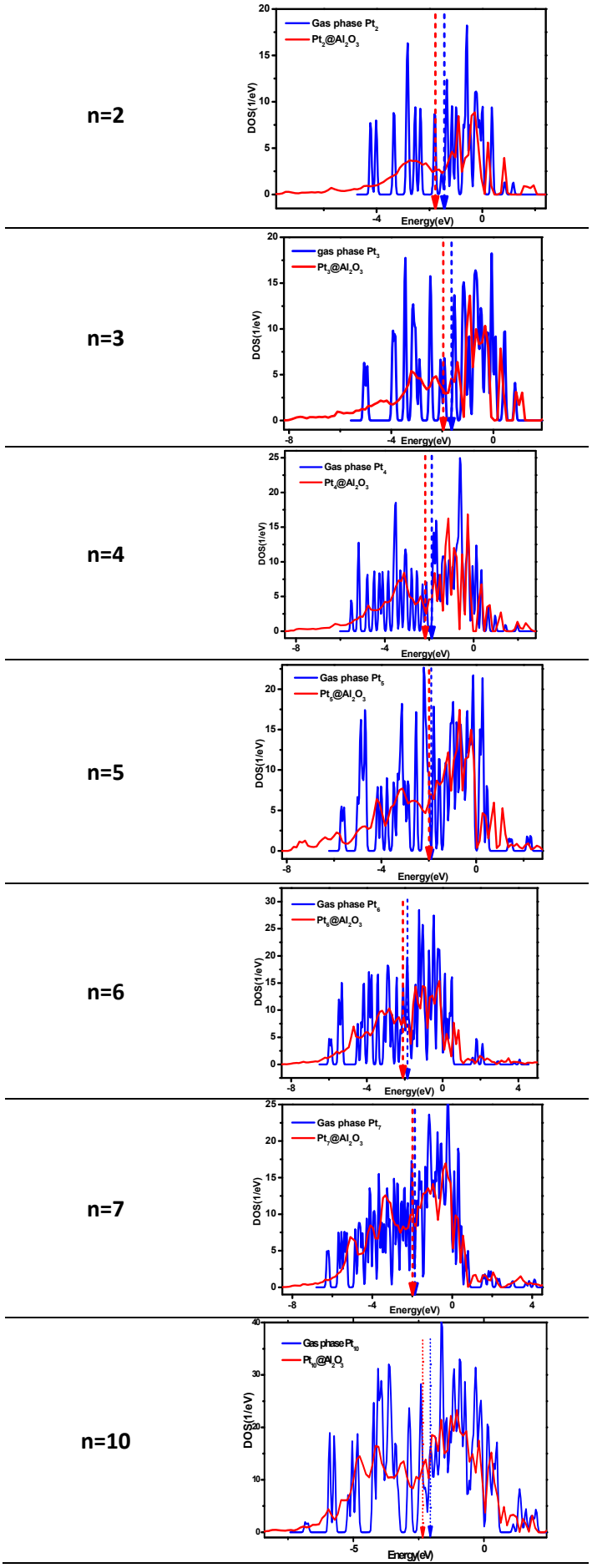

Figure-S6: Platinum-d orbital partial dos for free and Al_2O_3 supported Pt_n cluster. Arrows denote positions of corresponding d-band centers.

Table-S1: O-O Bond lengths (Å) in oxygen molecularly adsorbed on Pt_n cluster ($Pt_n + O_2 \rightarrow Pt_nO_2$)

n	Pt_n	$Pt_n@Al_2O_3$
1	1.41	1.40
2	1.41	1.40
3	1.42	1.43
4	1.42	1.42
5	1.44	1.43
6	1.43	1.43
7	1.40	1.42
10	1.44	1.45

Note: O-O bond length in oxygen molecularly adsorbed on Pt(111) surface [$Pt(111)O_2$] is 1.43 Å

Table-S2: Pt-O Bond lengths (Å) of in oxides of Pt_n cluster ($Pt_n + O_2 \rightarrow O\text{-}Pt_n\text{-}O$)

Cluster Size(n)	O-Pt_n-O	O-supported Pt_n-O	Relative (%) elongation for supported cluster
1	1.73 Å	1.87 Å	8.09 %
2	1.80 Å	1.92 Å	6.67%
3	1.84 Å	1.89 Å	2.72%
4	1.90 Å	1.96 Å	3.16%
5	1.90 Å	1.96 Å	3.16%
6	1.90 Å	1.97 Å	3.68%
7	1.90 Å	1.98 Å	4.21%
10	1.91 Å	2.07 Å	8.38%

Note: Pt-O bond length in oxide of Pt(111) surface [O-Pt(111)-O] is 2.09 Å

Table-S3: Bader charge on platinum atom of supported Platinum cluster ($Pt_n@Al_2O_3$) before and after oxidation.

Cluster Size(n)	Charge on Pt in $Pt_n@Al_2O_3$	Charge on Pt in [O-($Pt_n@Al_2O_3$)-O]
1	-0.37e	1.32e
2	-0.56e	1.12e
3	-0.78e	0.71e
4	-0.90e	0.75e
5	-1.12e	0.50e
6	-1.20e	0.51e
7	-1.24e	0.48e
10	-1.15e	0.33e

Table-S4: Relaxation in z-coordinate of $Pt_n@Al_2O_3$ cluster after oxidation [O- ($Pt_n@Al_2O_3$)-O]. The relaxation has been calculated by taking the average of z-coordinate of supported cluster before and after oxidation. The negative sign in relaxation means reduction in z-coordinate, movement towards surface (reduction in distance between cluster and surface)

Cluster Size (n)	% Relaxation in z - coordination
2	-1.75 %
3	-2.45%
4	-1.31%
5	-4.37%
6	-2.37%
7	-4.57%
10	-2.35%