Supplementary material

for

Influence of hydroxylation on binding of PtSn cluster on γ-Al2O3 surfaces: A DFT study

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Figure S1. Top view of hydrated models of γ-Al2O3(110) surface(1x1). These models are denoted as snm, where n represents the equivalent of water molecules on the surface, and m represents the thermodynamic ranking of the individual functionalization mode at each OH coverage.

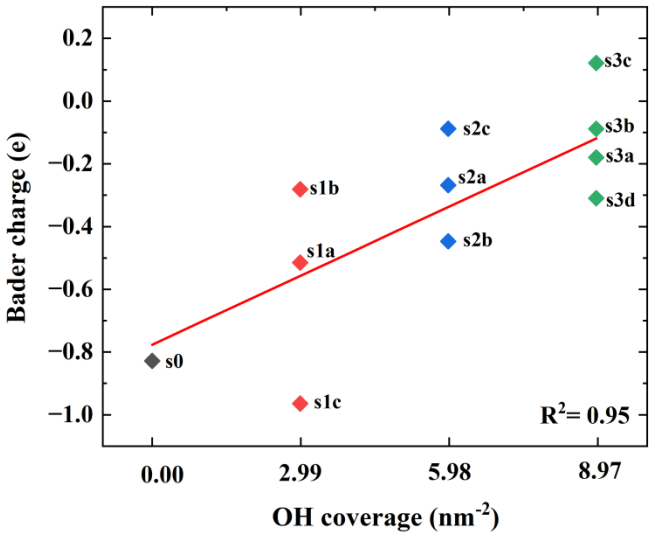

Figure S2. Bader charge of $Pt_{10}Sn_3$ clusters on γ-Al_2O_3(110) surfaces as a function of hydroxyl coverage.

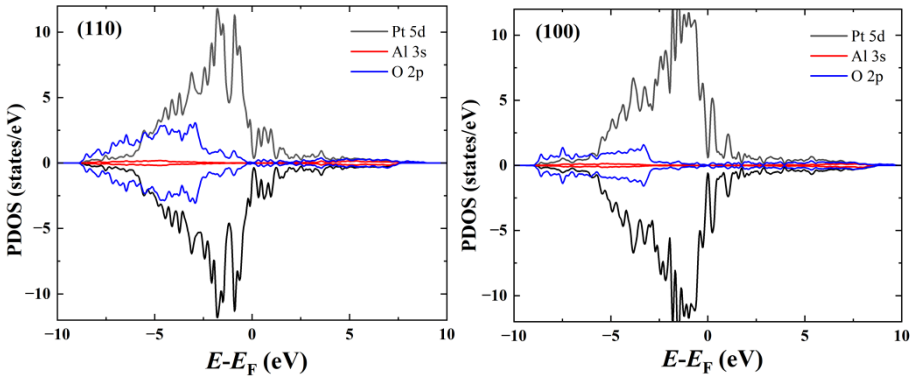

Figure S3. Projected density of states (PDOS) analysis of the atoms involved in the interaction between dehydrated γ-Al2O3 surfaces (left: (110) right: (100)) and the PtSn cluster.

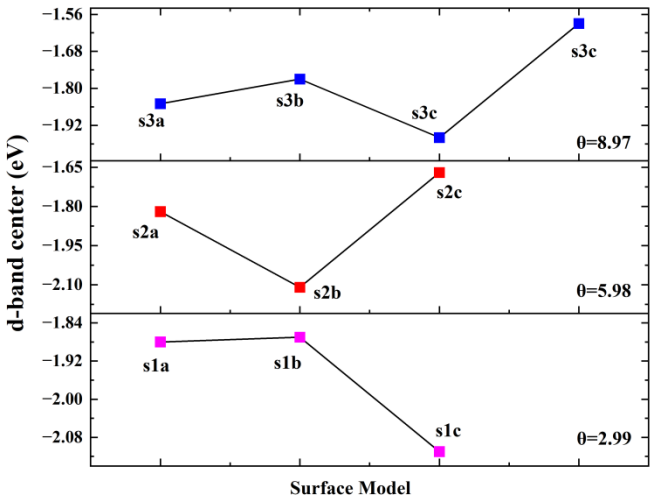

Figure S4. Variation of Pt d-band center with different types of hydroxyl groups on the γ-alumina (110) surface.

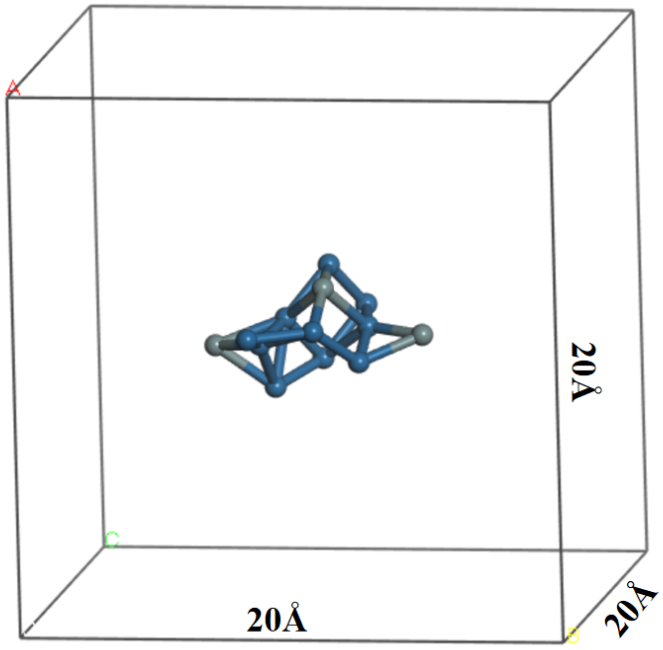

Figure S5. Structure for Pt10Sn3 isolated cluster.

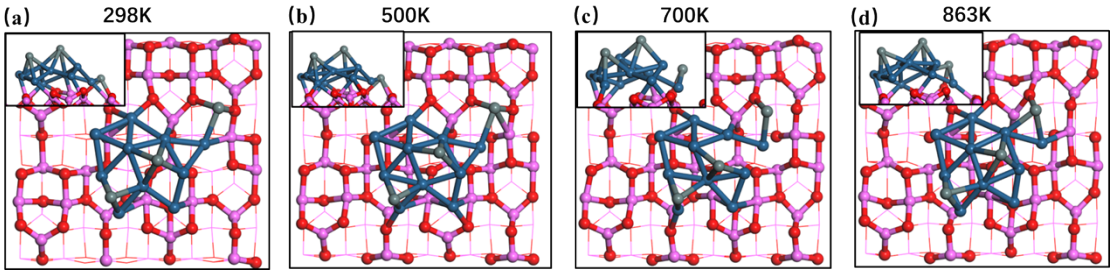

Figure S6. Structural evolution of Pt10Sn3/γ-Al2O3(110) during thermal treatment.

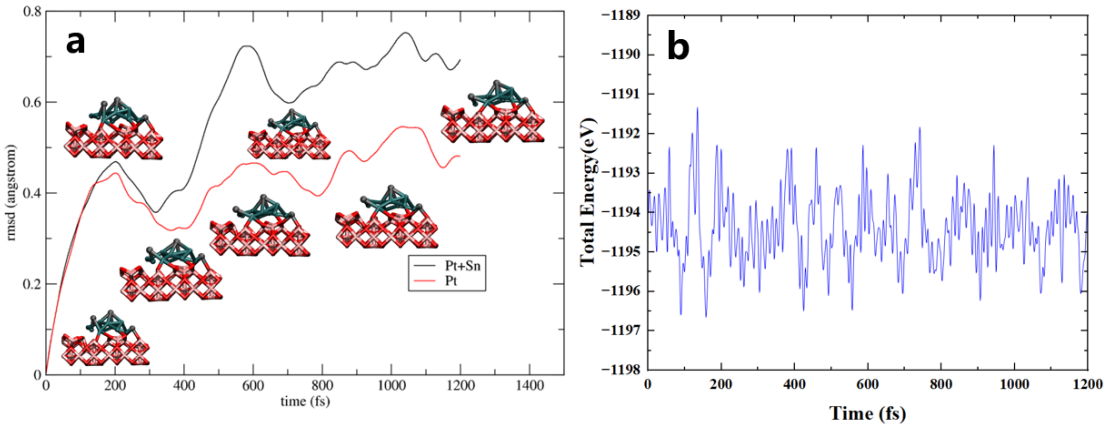

Figure S7. (a) The atomic positional RMSD of the PtSn cluster (black curve, rmsd of Pt atoms is also shown in red curve for comparison) and (b) the energy as a function of simulation time in the

simulation of Pt10Sn3/γ-Al2O3(110) at 863 K. The sideviews of the snapshots at the start, 200, 400, 600, 700, 1000, and 1200 fs are shown. The calculations indicate that at 863 K, the motion of Sn atoms (max. rmsd of ~ 1 angstrom, not shown for simplicity) is much more significant than the Pt atoms.

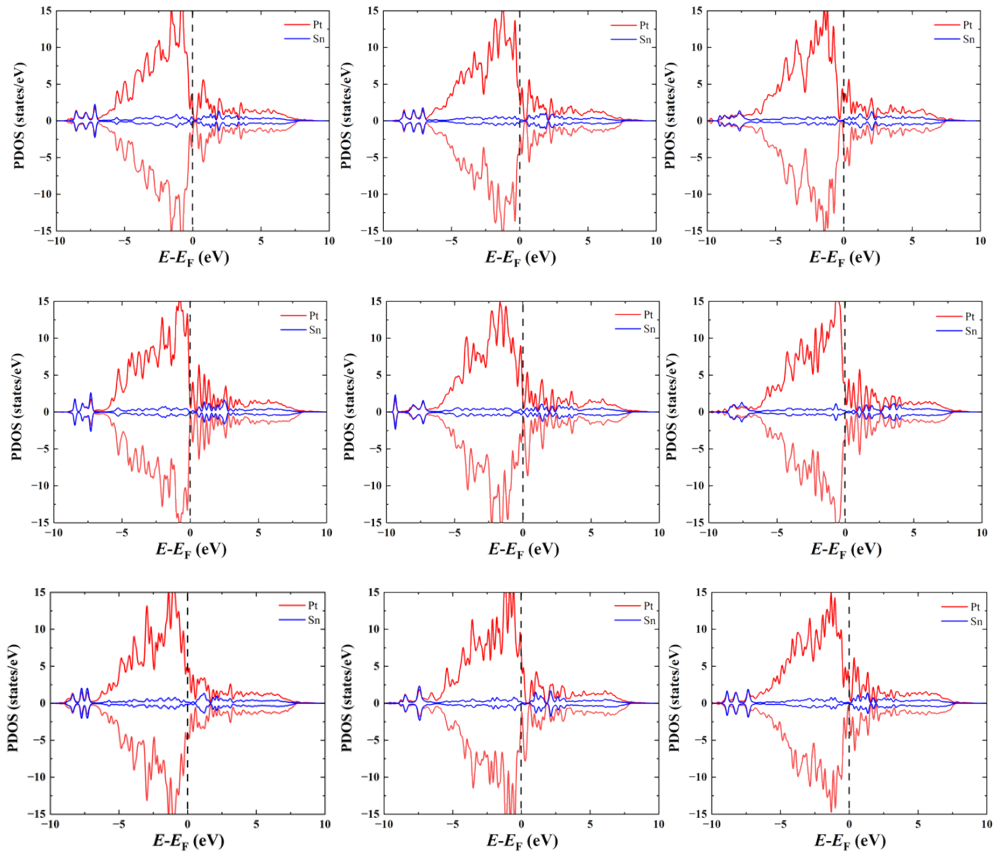

Figure S8. The PDOS of Pt and Sn atoms in the s1 (top, in the order of a,b,c), s2 (middle, in the order of a, b,c), and s3 (bottom, in the order of a, b,c) models.

Table S1. Energy statistics of hydroxylation model at different coverages. (All energies are referenced to the most stable system, where μ1 and μ2 represent the number of hydroxylated bonds to Al.)

θ=2.99 OH nm-2	μ1:μ2	ΔE/eV	θ=5.98 OH nm-2	μ1:μ2	ΔE/eV	θ=8.97 OH nm-2	μ1:μ2	ΔE/eV
s1a	1:0	0	s2a	1:1	0.85	s3a	2:1	0
s1b	0:1	2.43	s2b	1:1	1.03	s3b	2:1	1.13
s1c	1:0	0.84	s2c	2:0	0	s3c	3:0	0.12
						s3d	2:1	0.06

Table S2. d-band center values of Pt atoms on different hydroxylated model surfaces.

Model	d-band center (eV)
s1a	-1.88
s1b	-1.87
s1c	-2.11
s2a	-1.82
s2b	-2.11
s2c	-1.67
s3a	-1.85
s3b	-1.77
s3c	-1.96
s3d	-1.59

Table S3. Crystallographic structure of bulk γ -Al_2O_3

Property	Calc. (this work)	Ref.[1]
Cell parameters (a, b, c) (Å)	5.53, 8.34, 8.02	5.587, 8.413, 8.068
Cell volume ($Å^3/Al_2O_3$)	46.34	47.40

Table S4. Crystallographic structure of dehydrated γ-Al2O3(110) and (100) (b) surface models(1x1).

	a, b, c (Å)	atoms	$\sigma_{Surface\ energy}$ (J m^{-2})
γ-Al_2O_3(110)	8.34, 8.03, 24.89	40	1.97
γ-Al_2O_3(100)	5.54, 8.34, 21.38	40	1.23

Note: $\sigma_{Surface\ energy}$ = (2Eslab- Eunrelax-N*Ebulk)/S

Reference:

1 M. Digne, *Journal of Catalysis*, 2004, **226**, 54–68.