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

Supplementary Material

O_2 activation on subnanometer Re-Pt clusters supported on $TiO_2(110)$: exploring adsorption sites

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1. O_2 activation on $Pt_nRe_m(n+m=5)$ clusters supported on $TiO_2(110)$

Table S1: Bader charge analysis of supported Re_nPt_m clusters on $TiO_2(110)$. The charge for the cluster atoms is reported both before and after O_2 adsorption, as well as the difference between the two. The charges of the atoms are listed in order, starting with the Re atoms and continuing with the Pt atoms.

Supported Cluster	O_2 adsorption	Q[cluster atoms] (e)	Total cluster charge (e)
Re_5	Before	0.52, –0.07, 0.60, 0.48, 0.52	2.06
	After	0.52, 0.21, 0.97, 0.54, 0.82	3.06
	Difference	0.00, 0.28, 0.36, 0.06, 0.30	1.00
Re_4Pt_1	Before	0.42, 0.56, 0.75, 0.46, –0.45	1.74
	After	0.44, 1.18, 0.78, 0.47, –0.39	2.48
	Difference	0.02, 0.62, 0.03, 0.01, 0.06	0.74
Re_3Pt_2	Before	0.56, 0.91, 0.39, –0.33, –0.26	1.27
	After	0.81, 0.55, 1.14, –0.39, –0.41	1.70
	Difference	0.25, –0.36, 0.75, –0.06, –0.15	0.43
Re_2Pt_3	Before	0.84, 1.03, –0.31, –0.33, –0.08	1.15
	After	1.37, 1.15, –0.25, –0.36, –0.06	1.85
	Difference	0.53, 0.12, 0.06, –0.03, 0.02	0.70
Re_1Pt_4	Before	1.31, –0.25, –0.03, –0.22, –0.11	0.70
	After	1.31, –0.18, –0.21, 0.21, –0.04	1.09
	Difference	0.00, 0.07, –0.18, 0.43, 0.07	0.39
Pt_5	Before	–0.05, 0.15, 0.06, 0.00, 0.09	0.25
	After	–0.04, 0.42, 0.01, 0.31, 0.02	0.72
	Difference	0.01, 0.27, –0.05, 0.31, –0.07	0.47

Table S2: The adsorption of O_2 on the surface site of Re-Pt clusters supported on $TiO_2(110)$. The adsorption mode, adsorption energy (E_{ads}), and the height of the Ti atoms binding to the molecule are displayed.

Supported system	Adsorption mode	E_{ads}	Height-Ti_{5c}
Re_5	η^2−Ti	1.35	1.12
Re_4Pt_1	η^2−Ti	1.41	1.08
Re_3Pt_2	μ_2−Ti	1.55	0.00
Re_2Pt_3	η^2−Ti	1.32	1.10
Re_1Pt_4	μ_2−Ti	1.17	0.00
Pt_5	η^2−Ti	0.93	1.06

Table S3: Total charge transferred to the O_2 molecule (Q[O_2]), charge transferred from the cluster to the O_2 molecule (ΔQ[cluster]), and charge transferred from the surface to the O_2 molecule (ΔQ[surface]). The Bader charge is shown in e.

Sites	Charges	Re_5	Re_4Pt_1	Re_3Pt_2	Re_2Pt_3	Re_1Pt_4	Pt_5
Supported clusters	Q[O_2]	–0.99	–0.78	–0.62	–0.80	–0.44	–0.59
	ΔQ[cluster]	1.00	0.74	0.47	0.70	0.39	0.48
	ΔQ[surface]	–0.01	0.04	0.15	0.10	0.05	0.11
Surface	Q[O_2]	–0.94	–0.94	–0.88	–0.96	–0.89	–0.94
	ΔQ[cluster]	0.25	0.04	0.24	0.43	0.43	0.68
	ΔQ[surface]	0.69	0.90	0.64	0.53	0.46	0.26
Interface	Q[O_2]	–	–	–0.88	–0.83	–0.85	–0.83
	ΔQ[cluster]	–	–	0.47	0.66	0.68	0.62
	ΔQ[surface]	–	–	0.41	0.17	0.17	0.21

Table S4: The effect of the temperature (T = 300 K) on reaction energies for the O_2 dissociation on gas-phase Re-Pt clusters

Gas-phase clusters	Δ E [T = 0 K] (eV)	Δ G [T = 300 K] (eV)	Thermal Correction (eV)
Re5	-3.52	-3.50	0.02
Re4Pt1	-3.23	-3.35	-0.12
Re3Pt2	-2.87	-2.92	-0.05
Re2Pt3	-2.87	-2.92	-0.05
Re1Pt4	-2.84	-2.76	0.08
Pt5	-0.44	-0.50	-0.06

2. Structure and properties of $Pt_nRe_m(n+m=5)$ clusters supported on $TiO_2(110)$

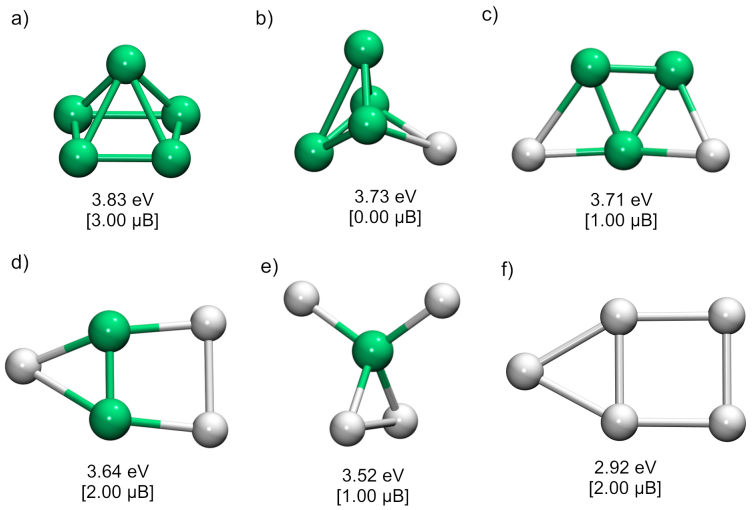


Figure S1: Global minima configurations for gas-phase $Re_nPt_m(n+m=5)$: a) Re_5, b) Re_4Pt_1, c) Re_3Pt_2, d) Re_2Pt_3, e) Re_1Pt_4, f) Pt_5. The binding energy and magnetization are shown below each structure.

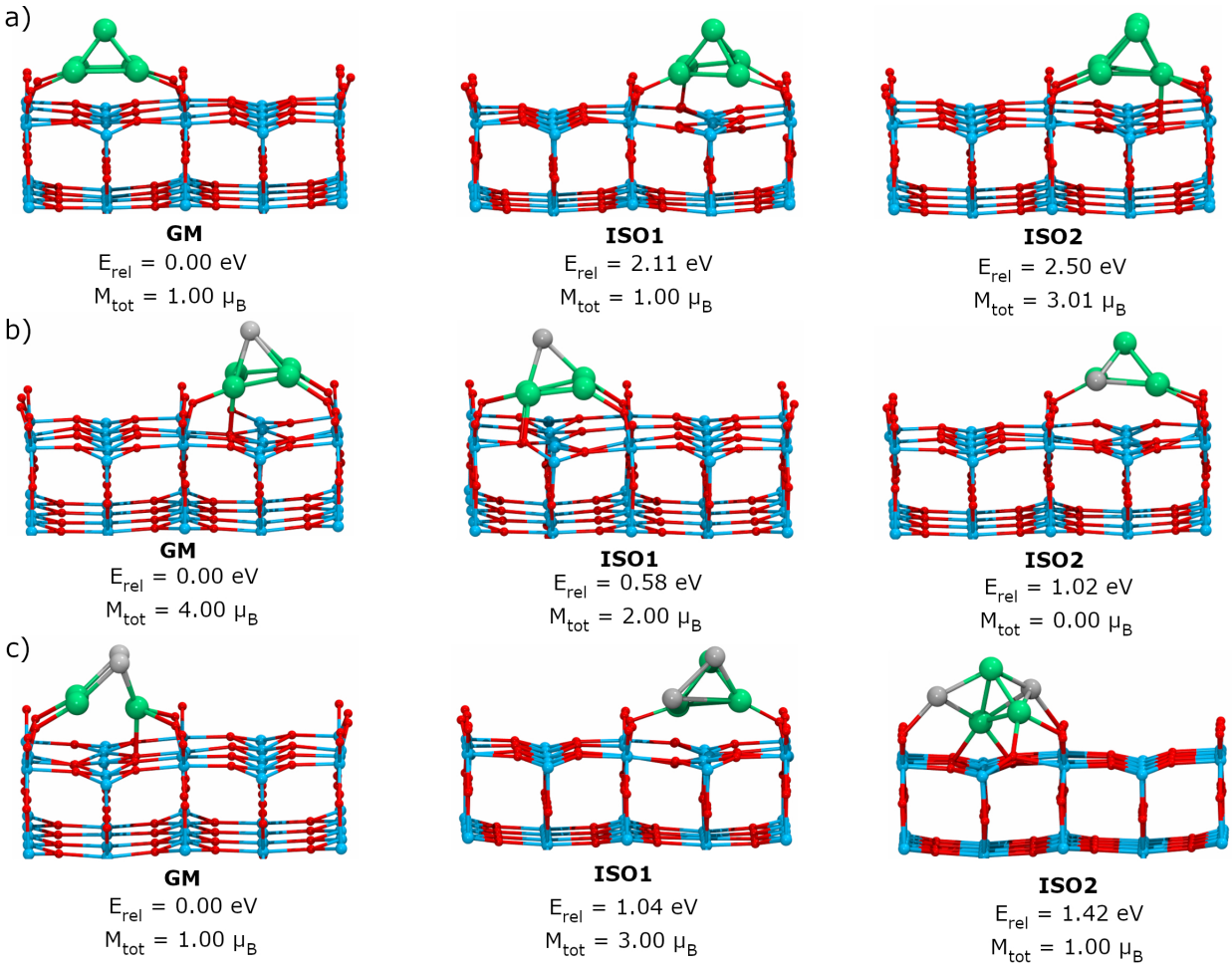
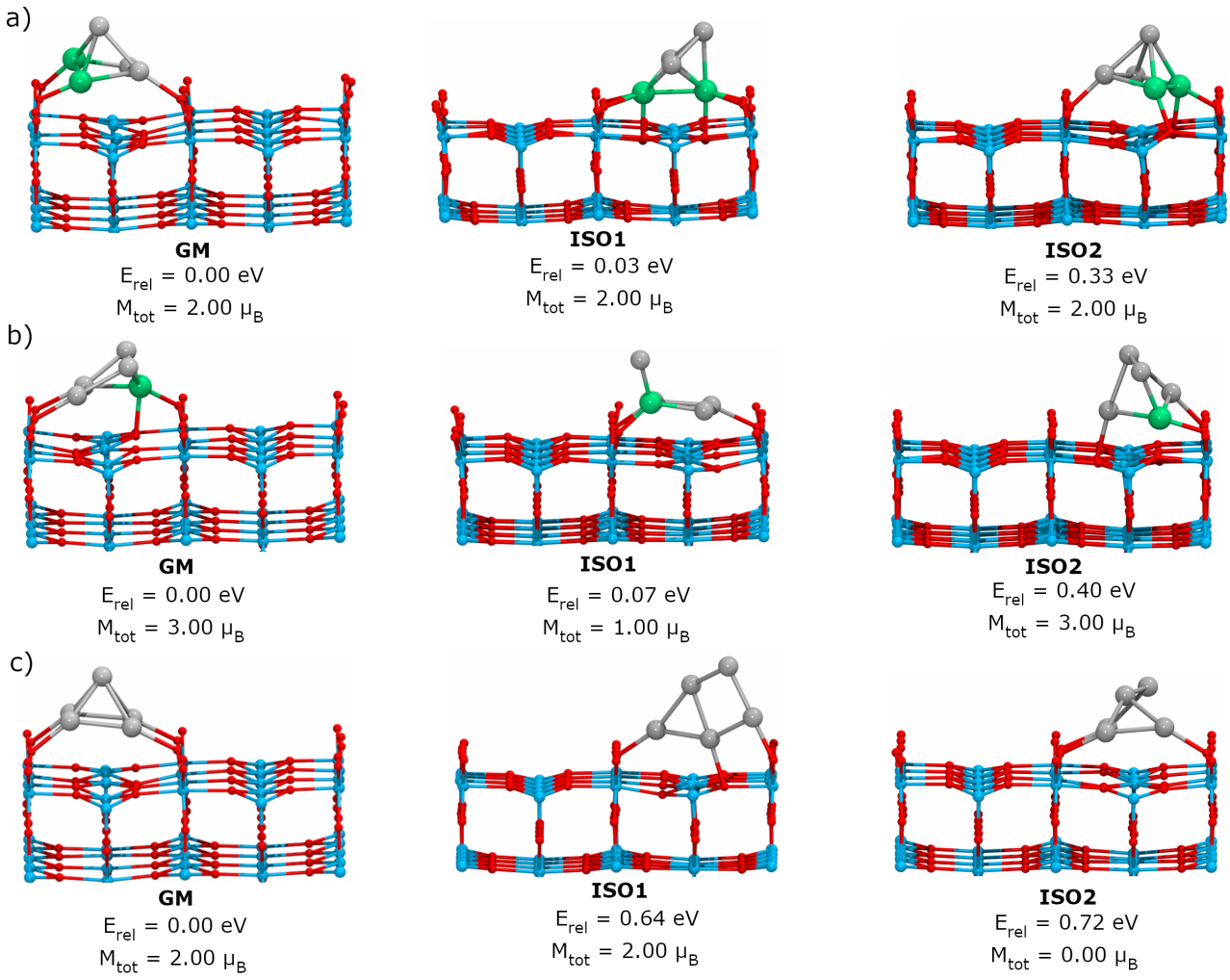


Figure S2: Putative global minima(GM) and lowest energy isomers(ISO1, ISO2) for a) Re_5, b) Re_4Pt_1, and c) Re_3Pt_2 clusters supported on $TiO_2(110)$. The relative energy and total magnetization are presented below each structure



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3. O_2 dissociation on $Pt_nRe_m(n+m=5)$ clusters supported on $TiO_2(110)$

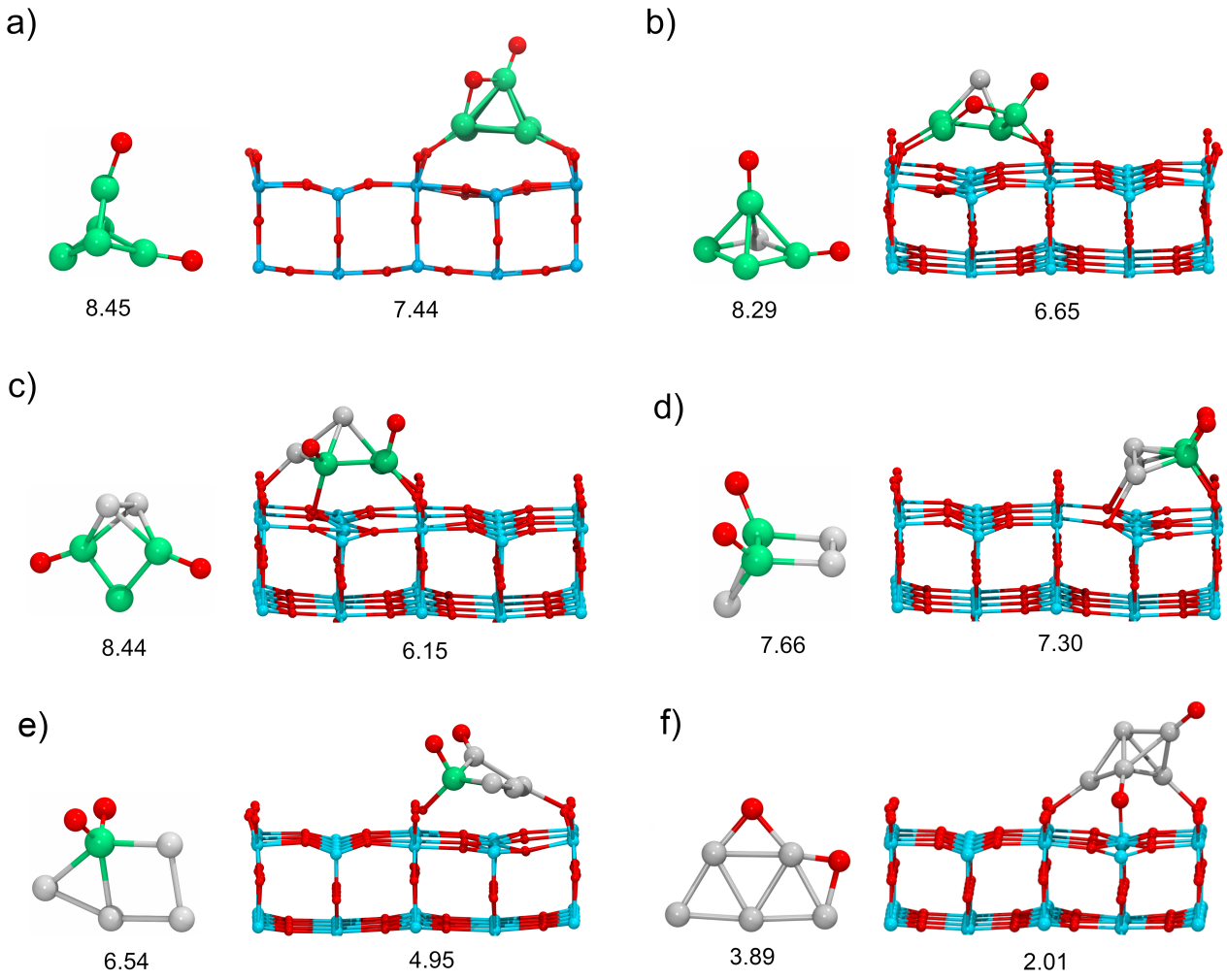


Figure S4: The most stable structures for O_2 dissociation on gas-phase (left) and supported (right) $Re_nPt_m(n+m=5)$ clusters : a) Re_5, b) Re_4Pt_1, c) Re_3Pt_2, d) Re_2Pt_3, e) Re_1Pt_4. The dissociative adsorption energy of O_2 is displayed below each structure in eV. The structure of the supported clusters is simplified by showing only the surface trilayer for ease of analysis.

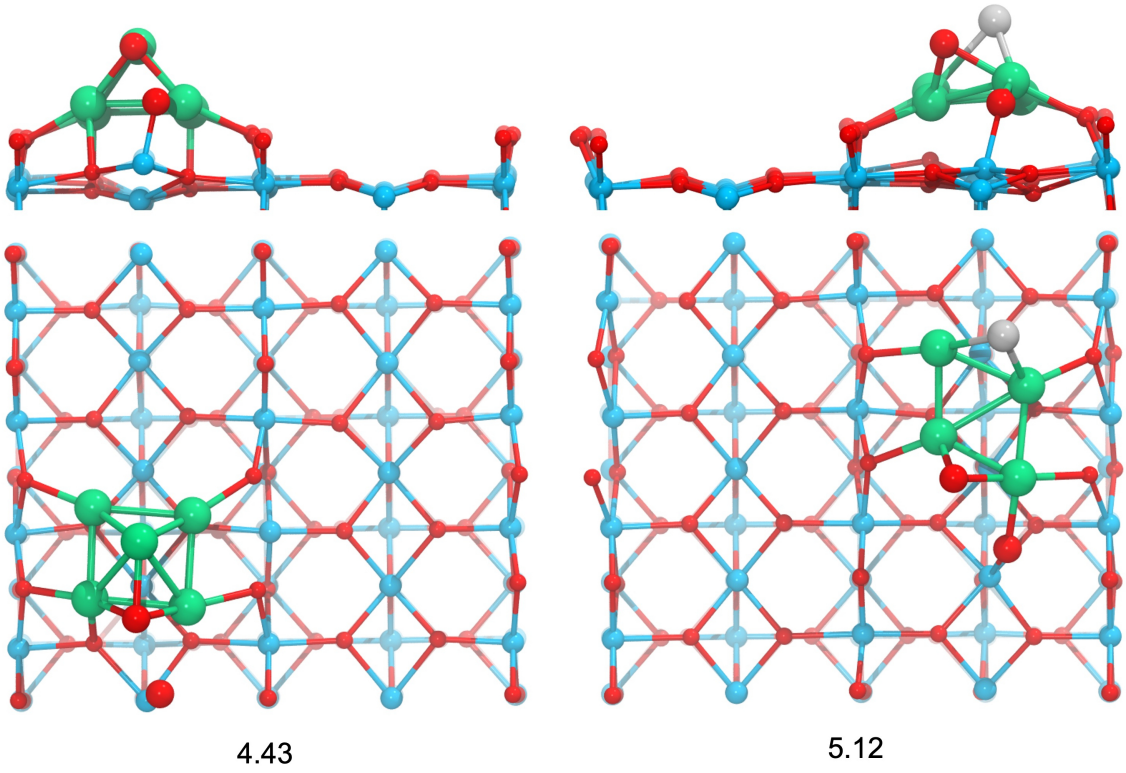
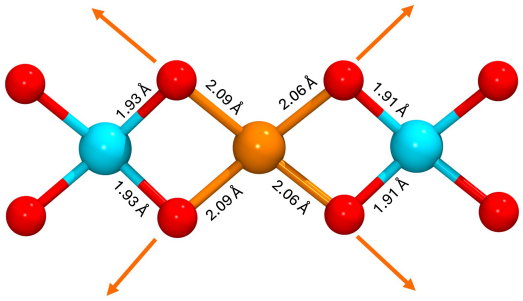


Figure S5: The most stable structures for dissociative adsorption on the interface Re-Ti of Re_5 (left) and Re_4Pt_1 (right) supported on $TiO_2(110)$ surface. Adsorption of O_2 at the Re-Ti interface is prone to dissociation, leading to the formation of atomic oxygen. The adsorption energy is displayed below each structure in eV.



Supported Cluster	Ti–O length (Å)
Re5	2.09, 2.09, 2.06, 2.06
Re4Pt1	2.10, 2.08, 2.08, 2.06
Re3Pt2	2.09, 2.06, 2.06, 2.06
Re1Pt4	2.09, 2.07, 2.06, 2.06

Figure S6: The lattice distortions caused by the formation of small polarons on the $TiO_2(110)$ surface. The left side shows the distortion for the substrate of the Re_5 cluster. The right side shows the Ti–O lengths for the lattice distortion of the Re-Pt clusters supported on $TiO_2(110)$.