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Translational dependence of the geometry of metallic mono- and bilayers optimized at semi-ionic supports. The cases of Pd at γ-Al_2O_3(110), monoclinic ZrO_2(001), and rutile TiO_2(001).

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TABLES 2

FIGURES 3

Table S1. Pd-O distances and final U_{Pd} values in the bilayer $Pd_{32}(111)$ slabs at the m-$ZrO_2(001)$ (Fig. S2).

U_{Pd} = -4.836	U_{Pd} = -4.920
2.125	2.174
2.126	2.164
2.208	2.137
2.207	2.138
2.125	2.159
2.125	2.150
2.208	2.156
2.208	2.164

Table S2. Relative stabilization energy (eV/Pd) per Pd atom U_{Pd} (1) for single atom, clusters (N = 24), (111) monolayers with vacancies (N = 24-28), full monolayers (N = 28, 30), bilayer (N = 36), and 4-layer Pd(110) (N = 72) deposited over $Al_{56}O_{80}$ model of γ-Al_2O_3(110) (-959.173/-972.443 eV), $Ti_{36}O_{72}$ model of TiO_2(001) surface (-931.47/-943.070 eV) and $Zr_{32}O_{64}$ model of m-ZrO_2(001) surface (-902.078/-914.999 eV) optimized at PBE/PBE-D3 levels.

System	N	-U		-U_{Pd}		Figure
		PBE	PBE-D3	PBE	PBE-D3	
γ-Al_2O_3						
Atom	1	964.487	978.080	5.314	5.637	S1g
		962.960	976.625	3.787	4.182	-
		962.928	976.592	3.755	4.149	-
		245.044[a)]	248.728	5.159	5.538	1b
1-layer	24	1075.617	1099.454	4.852	5.293	2a, b
		1076.438[b)]	1101.163	4.886	5.364	2c, d
		1073.141[c)]	1097.848	4.749	5.226	2e, f
		1076.671[d)]	1101.153	4.896	5.363	2g, h
	28	1094.895	1120.937	4.847	5.303	S4c
		1095.404[e)]	1121.211	4.865	5.313	-
		1095.295[f)]	1121.491	4.862	5.323	3h
	30	1105.119	1132.106	4.865	5.322	3i
2-layer(100)	48	1196.118[g)]	1231.586	4.936	5.399	1c
		1196.352[e, g)]	1231.607	4.941	5.399	-
TiO_2						
Atom	1	934.788	946.878	3.318	3.81	S1a
		934.581	946.683	3.111	3.69	S1b
		934.196	946.370	2.726	3.39	S1c
Cluster	24	1034.136	1056.228	4.278	4.715	1e
1-layer (111)	24	1029.716	1053.657	4.094	4.608	S1d
	24[f)]	1029.174	1052.945	4.071	4.578	S1e
	24[h)]	1032.018	1055.457	4.190	4.683	4f
	27	1046.584	1071.924	4.263	4.295	4d, e
	28	1051.996	-	4.305	-	6a
	30	1072.773	1099.998	4.710	5.23	4g,h
	30[f)]	1062.322	1089.401	4.362	4.878	4i, j
	32	1070.756	-	4.353	-	S3b
2-layer(111)	48	1153.110	1187.298	4.618	5.088	S1f
4-layer (110)	72	1270.856	1316.895	4.714	5.192	1f
m-ZrO_2						
Atom	1	906.345	-	4.267	-	S1h
1-layer	16	970.783[i)]	991.707	4.294	4.794	5a
		969.970[j)]	991.059	4.243	4.754	-
		971.278[g)]	992.182	4.325	4.824	-
		971.459[k)]	992.492	4.336	4.843	5b, c
		971.455[l)]	992.485	4.336	4.843	5d
2-layer (111)	32[m)]	597.438[g)]	617.927	4.920	5.417	S2b
		594.750[g)]	614.605	4.836	5.313	S2a

[a)] for smaller UC such as $Al_{14}O_{20}$ (-239.885/-243.190 eV, see text); [b)] after shift by 1 Å along OY direction; [c)] after shift by 2 Å along OY direction; [d)] after shift by 3 Å along OY direction; [e)] shift by 1 Å along both OX and OY directions; [f)] shift by 1 Å along OX direction; [g)] (111) model; [h)]

"band" type structure; [i] 1/1 model; [j] (100) model; [k] 4R-4R model; [l] "mix" model; [m] thin $Zr_{16}O_{32}$ support model (-440.002/-444.576 eV).

Figure captions

Figure S1. (a-c, g, h) Single Pd atoms, (d-e) Pd_{24} monolayers, (f) Pd_{48} bilayer at (a-f) $Ti_{36}O_{72}$ model of rutile $TiO_2(001)$, (g) $Al_{56}O_{80}$ model of γ-$Al_2O_3(110)$, (h) $Zr_{32}O_{64}$ model of m-$ZrO_2(001)$ surfaces optimized at the PBE level. The stabilization energy per Pd atom U_{Pd} is given in eV/Pd. The atomic colors are given in red, magenta, green, cyan light, and gray for O, Al, Ti, Zr, and Pd, respectively.

Figure S2. Upper projection of $Pd_{32}(111)$ bilayers at $Zr_{32}O_{64}$ model of m-$ZrO_2(001)$ surfaces optimized at the PBE level. The stabilization energy U_{Pd} per Pd atom is given in eV/Pd. The atomic color agreement corresponds to Fig. S1.

Figure S3. (a, b) Side and (c) upper projection of (a) as deposited (non-optimized) $Pd_{32}(100)$, optimized (b) Pd_{32} and (c) $Pd_{28}(111)$ monolayers at $Ti_{36}O_{72}$ model of m-$TiO_2(001)$ surfaces optimized at the PBE level. The stabilization energy U_{Pd} per Pd atom is given in eV/Pd. Di-vacancy is shown by ellipse (c). The atomic color agreement corresponds to Fig. S1.

Figure S1

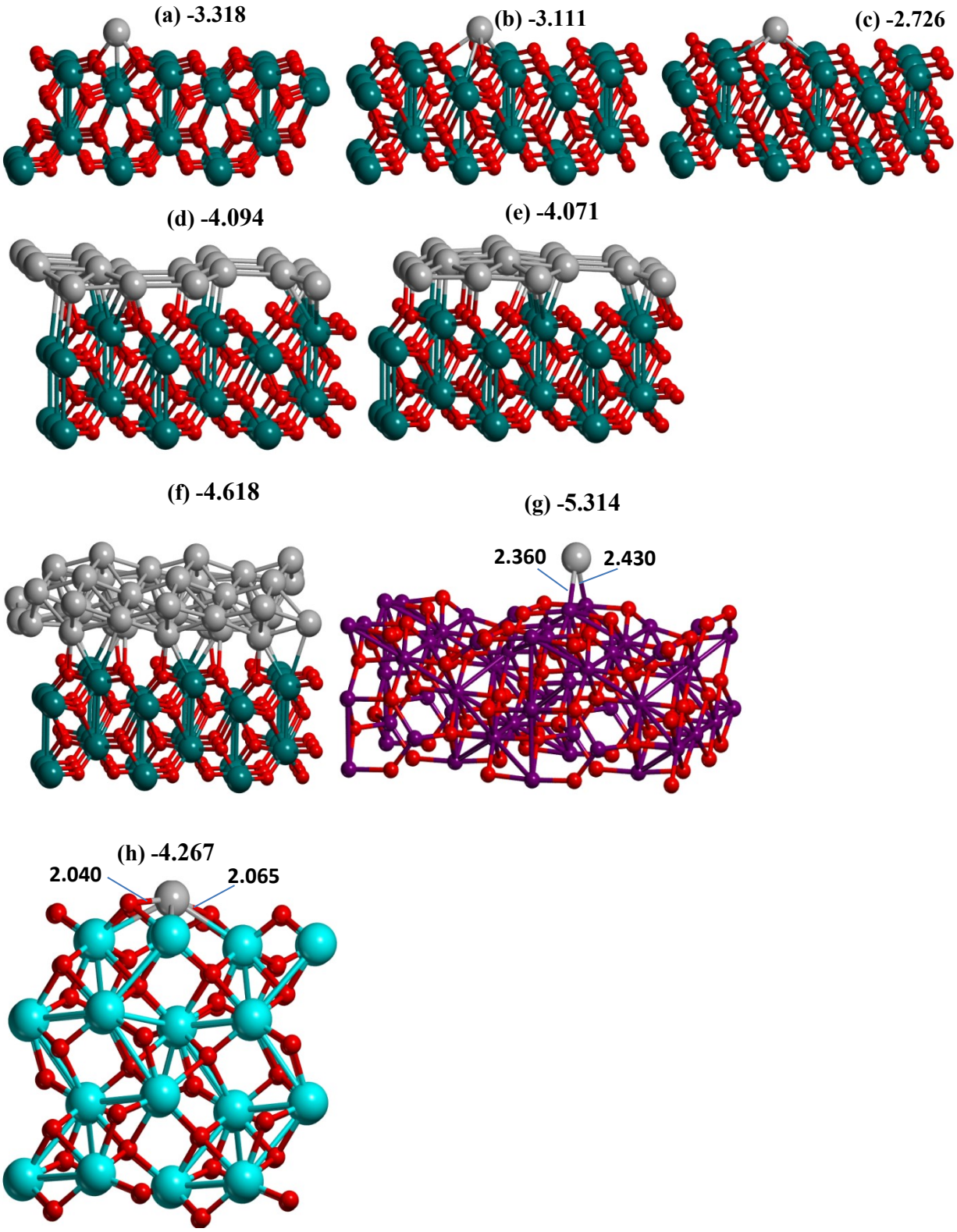
(a) -3.318
(b) -3.111
(c) -2.726
(d) -4.094
(e) -4.071
(f) -4.618
(g) -5.314
2.360
2.430
(h) -4.267
2.040
2.065

Figure S2

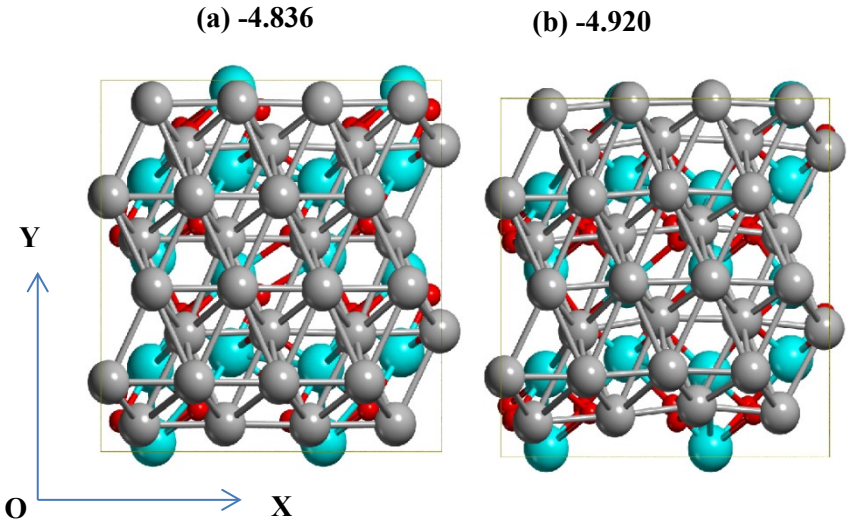

Figure S3