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Supplementary Information

Effects of oxygen coverage, catalyst size, and core composition on Pt-alloy core-shell nanoparticles for the oxygen reduction reaction

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Notation

E_{sys}= energy of the selected system (eV)

$E_{O/sys}$= energy of the oxygen-adsorbed selected system (eV)

$E_{ads,sys}$ = adsorption energy of oxygen atom on the selected system (eV)

$E_{seg(A-B)}$ = segregation energy of the system of A and B segregated pair (eV/atom/pair)

$E_{dis,sys}$ = dissolution energy of the selected system (eV)

$E_{sys,0}$ = energy of the system before dissolution (eV)

$E_{sys,+}$ = energy of the system after dissolution (eV)

ΔE_{dis} = dissolution energy shift of the system from pure Pt system (eV)

$E_{dis,alloy}$ = dissolution energy of the core-shell system (eV)

$E_{dis,Pt}$ = dissolution energy of the pure Pt system (eV)

Table I. Adsorption energy of the 116-atom Pt_{shell}-$(M\text{-}Ni)_{core}$ nanoparticle system.

Pt_{shell}-$(M\text{-}Ni)_{core}$	E_{sys} (eV)	$E_{O/sys}$ (eV)	E_{ads} (sys) (eV)	E_{ads}(Pt) (eV)	$E_{ads,rel}$ (eV/atom)
Fe	-708.46	-712.65	0.72	-1.23	+1.95
Co	-664.58	-670.02	-0.53	-1.23	+0.70
Ru	-725.96	-731.50	-0.63	-1.23	+0.60
Rh	-660.92	-666.64	-0.80	-1.23	+0.43
Re	-838.57	-844.22	-0.73	-1.23	+0.50
Os	-786.29	-791.87	-0.66	-1.23	+0.57
Ir	-705.70	-711.48	-0.86	-1.23	+0.37

Table II. Oxygen adsorption energy of Ptshell-(Re-Ni)core system as a function of sized and oxygen coverage and Ptshell-(Fe-Cn-Fe-Ni)core system as a function of carbon content and oxygen coverage per (111) facet. The adsorption sites are defined as in Figure 3.

The label of the adsorption site of E and NE specifies that for the E (Edge) one of the oxygen atoms is adsorbed on the site near the edge of the nanoparticle, while for NE (non-Edge) means that all of the adsorbed oxygen are not located at the site near the edge.

# total atoms	# O-atoms /O-Coverage	Adsorption site	E_{sys} (eV)	$E_{O/sys}$ (eV)	E_{ads} (eV/atom)	$E_{ads,rel}$ (eV)
		Pt_{shell}-$(Re\text{-}Ni)_{core}$				
116 (NP**)	1 (0.0128 ML)	Def	-838.57	-844.236	-0.74	-
		A	-838.57	-844.238	-0.75	-
		B	-838.57	-844.239	-0.75	+0.49
	2 (0.0256 ML)	Def & A	-838.57	-849.85	-0.73	-
		Def & B	-838.57	-849.86	-0.73	+0.45
		A & B	-838.57	-849.84	-0.72	-
	8 (0.103 ML)*	Def*	-838.57	-882.58	-0.59	+0.59
260 (NP**)	1 (0.007 ML)	A	-1933.92	-1939.68	-0.84	-
		B	-1933.92	-1939.44	-0.60	-
		C	-1933.92	-1939.69	-0.85	-
		D	-1933.92	-1939.82	-0.98	+0.07
		E	-1933.92	-1939.45	-0.61	-
		F	-1933.92	-1939.68	-0.85	-
		G	-1933.92	-1939.50	-0.66	-
	2 (0.014 ML)	E01 (A+B)	-1933.92	-1944.97	-0.61	-
		E02 (A+C)	-1933.92	-1945.18	-0.71	+0.39
		E03 (C+F)	-1933.92	-1944.80	-0.53	-
		E04 (F+G)	-1933.92	-1944.99	-0.62	-
		NE1 (A+D)	-1933.92	-1945.14	-0.69	-
		NE2 (B+D)	-1933.92	-1944.96	-0.60	-
		NE3 (C+D)	-1933.92	-1945.14	-0.69	-
		NE4 (F+D)	-1933.92	-1944.93	-0.59	-
	8 (0.056 ML)*	A*	-1933.92	-1978.88	-0.70	+0.40
45 (SLAB)	1 (0.111 ML)	P1	-299.49	-305.007	-0.599	-
		P2	-299.49	-305.008	-0.600	+0.67
		P3	-299.49	-305.007	-0.599	-
		P4	-299.49	-305.007	-0.599	-
		Pt_{shell}-$(Fe\text{-}C_n\text{-}Fe\text{-}Ni)_{core}$* **				
284 ($Fe_{4.6}C_{1.0}$) †	1 (0.007 ML)	Def	-1929.44	-1937.66	-3.30	-2.07
296 ($Fe_{3.1}C_{1.0}$) †		Def	-2035.20	-2042.31	-2.19	-0.95
302 ($Fe_{2.6}C_{1.0}$) †		Def	-2085.00	-2091.69	-1.77	-0.53
310 ($Fe_{2.2}C_{1.0}$) †		Def	-2154.09	-2157.93	+1.07	+2.30

*For the system of 8 oxygen atoms, 1 oxygen atom per (111) facet is adsorbed at the designated position, where each nanoparticle has eight (111) facets.

**NP = nanoparticle model

*** For Pt_{shell}-$(Fe\text{-}C_n\text{-}Fe\text{-}Ni)_{core}$, all systems are nanoparticles

Highlight = selected system of the most stable configuration at each oxygen coverage

† the composition of the core-anchoring shell as Fe_xC_y

Table III. Segregation energy for Pt_{shell}-$(Re\text{-}Ni)_{core}$ as a function of sizes and oxygen coverage and for Pt_{shell}-$(Fe\text{-}Cn\text{-}Fe\text{-}Ni)_{core}$ as a function of carbon content and oxygen coverage Definitions of the sites are in Figure 3.

# total atoms	# O-atoms /O-Coverage	Adsorption site	E_{sys} (eV)	E_{NS} (eV)	E_{seg} (Pt-M)* (eV/atom/pair)	E_{seg} (Re-Ni) (eV/atom/pair)
Pt_{shell}-$(Re\text{-}Ni)_{core}$						
116 (NP**)	1 (0.0128 ML)	Def	-838.57	-844.24	-1.36	N/D
		A	-838.57	-844.24	-7.20	N/D
		B	-838.57	-844.24	-6.52	-0.126
	2 (0.0256 ML)	Def & A	-838.57	-849.85	-0.394	N/D
		Def & B	-838.57	-849.86	-0.22	-0.013
		A & B	-838.57	-849.84	-0.397	N/D
	8 (0.103 ML)‡	Def	-838.57	-882.58	-0.27	+0.11
260 (NP**)	1 (0.007 ML)	A	-1933.92	-1939.68	N/D	N/D
		B	-1933.92	-1939.44	N/D	N/D
		C	-1933.92	-1939.69	N/D	N/D
		D	-1933.92	-1939.82	-1.06	-0.566
		E	-1933.92	-1939.45	N/D	N/D
		F	-1933.92	-1939.68	N/D	N/D
		G	-1933.92	-1939.5	N/D	N/D
	2 (0.014 ML)	E01 (A+B)	-1933.92	-1944.97	N/D	N/D
		E02 (A+C)	-1933.92	-1945.18	-0.80	-0.147
		E03 (C+F)	-1933.92	-1944.8	N/D	N/D
		E04 (F+G)	-1933.92	-1944.99	N/D	N/D
		NE1 (A+D)	-1933.92	-1945.14	N/D	N/D
		NE2 (B+D)	-1933.92	-1944.96	N/D	N/D
		NE3 (C+D)	-1933.92	-1945.14	N/D	N/D
		NE4 (F+D)	-1933.92	-1944.93	N/D	N/D
45 (SLAB)	1 (0.111 ML)	P1	-299.49	-305.007	-1.642	N/D
		P2	-299.49	-305.008	-1.640	-1.113
		P3	-299.49	-305.007	-1.957	N/D
		P4	-299.49	-305.007	-1.645	N/D
	1 (0.25 ML)	Def****	-128.8	-138.72	-0.93	-0.481
Pt_{shell}-$(Fe\text{-}C_n\text{-}Fe\text{-}Ni)_{core}$* **						
272 ($Fe_{9.2}C_{1.0}$)†	0 (0 ML)	Def	-1823.07	-1823.07	-1.32	N/D
284 ($Fe_{4.6}C_{1.0}$)†		Def	-1929.44	-1929.44	-0.56	N/D
296 ($Fe_{3.1}C_{1.0}$)†		Def	-2035.20	-2035.20	-0.61	N/D
310 ($Fe_{2.2}C_{1.0}$)†		Def	-2154.09	-2154.09	+2.24	N/D
284 ($Fe_{4.6}C_{1.0}$)†	1 (0.007 ML)	Def	-1929.44	-1937.66	+1.08	N/D
296 ($Fe_{3.1}C_{1.0}$)†		Def	-2035.20	-2042.31	-0.02	N/D
302 ($Fe_{2.6}C_{1.0}$)†		Def	-2085.00	-2091.69	+0.53	N/D
310 ($Fe_{2.2}C_{1.0}$)†		Def	-2154.09	-2157.93	+0.10	N/D

*M = Re for Pt_{shell}-$(Re\text{-}Ni)_{core}$ and M = Fe for Pt_{shell}-$(Fe\text{-}C_n\text{-}Fe\text{-}Ni)_{core}$

NP = nanoparticle model * all systems are nanoparticles

****This adsorption site is at the same position as P1 in 0.111 ML system

‡For the system of 8 oxygen atoms, 1 oxygen atom per (111) facet is adsorbed at the designated position, where each nanoparticle has eight (111) facets.

Highlight = selected system of the most stable configuration at each oxygen coverage

† = the composition of the core-anchoring shell as Fe_xC_y

Table IV. Dissolution potential shift for $Pt_{shell}(Re\text{-}Ni)_{core}$ nanoparticles as a function of sizes and Pt_{shell}-(Fe-C_n-Fe-Ni)$_{core}$ nanoparticles as a function of carbon content Definitions of the sites are in Figure 9.

# total atoms	Adsorption site	$E_{sys,0}$ (eV)	$E_{sys,+}$ (eV)	$E_{dis,alloy}$(eV)	$E_{dis,Pt}$ (eV)	ΔE_{dis} (eV)
			$Pt_{shell}(Re\text{-}Ni)_{core}$			
116 (NP**)	IP	-838.57	-831.58	-6.98	-6.64	-0.34
	ED1	-838.57	-832.22	-6.35	-5.98	-0.37
	ED2	-838.57	-831.92	-6.65	-6.24	-0.42
260 (NP**)	IP1	-1933.92	-1927.27	-6.65	-6.62	-0.03
	IP2	-1933.92	-1926.74	-7.18	-6.92	-0.26
	IP3	-1933.92	-1927.07	-6.86	-6.91	+0.05
	IP4	-1933.92	-1927.26	-6.67	-6.63	-0.04
	ED1	-1933.92	-1927.01	-6.92	-6.32	-0.60
	ED2	-1933.92	-1927.73	-6.20	-5.89	-0.30
	ED3	-1933.92	-1926.97	-6.95	-6.31	-0.64
	ED4	-1933.92	-1927.22	-6.70	-6.32	-0.38
45 (SLAB)	P1	-299.49	-292.23	-7.26	-7.29	+0.03
	P2	-299.49	-292.24	-7.26	-7.29	+0.04
	P3	-299.49	-292.23	-7.26	-7.29	+0.03
	P4	-299.49	-292.23	-7.26	-7.29	+0.03
			Pt_{shell}-(Fe-C_n-Fe-Ni)$_{core}$***			
272 ($Fe_{9.2}C_{1.0}$)†	IP2	-1823.07	-1817.13	-5.94	-6.92	+0.97
284 ($Fe_{4.6}C_{1.0}$)†	IP2	-1929.44	-1923.68	-5.76	-6.92	+1.16
296 ($Fe_{3.1}C_{1.0}$)†	IP2	-2035.20	-2028.69	-6.52	-6.92	+0.40
302 ($Fe_{2.6}C_{1.0}$)†	IP2	-2085.00	-2077.33	-7.68	-6.92	-0.76
310 ($Fe_{2.2}C_{1.0}$)†	IP2	-2154.09	-2146.81	-7.28	-6.92	-0.36

**NP = nanoparticle

*** all systems are nanoparticles

† the composition of the core-anchoring shell as Fe_xC_y