A DFT study on the O_2 adsorption properties of supported PtNi clusters

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Supplementary Materials

Figures

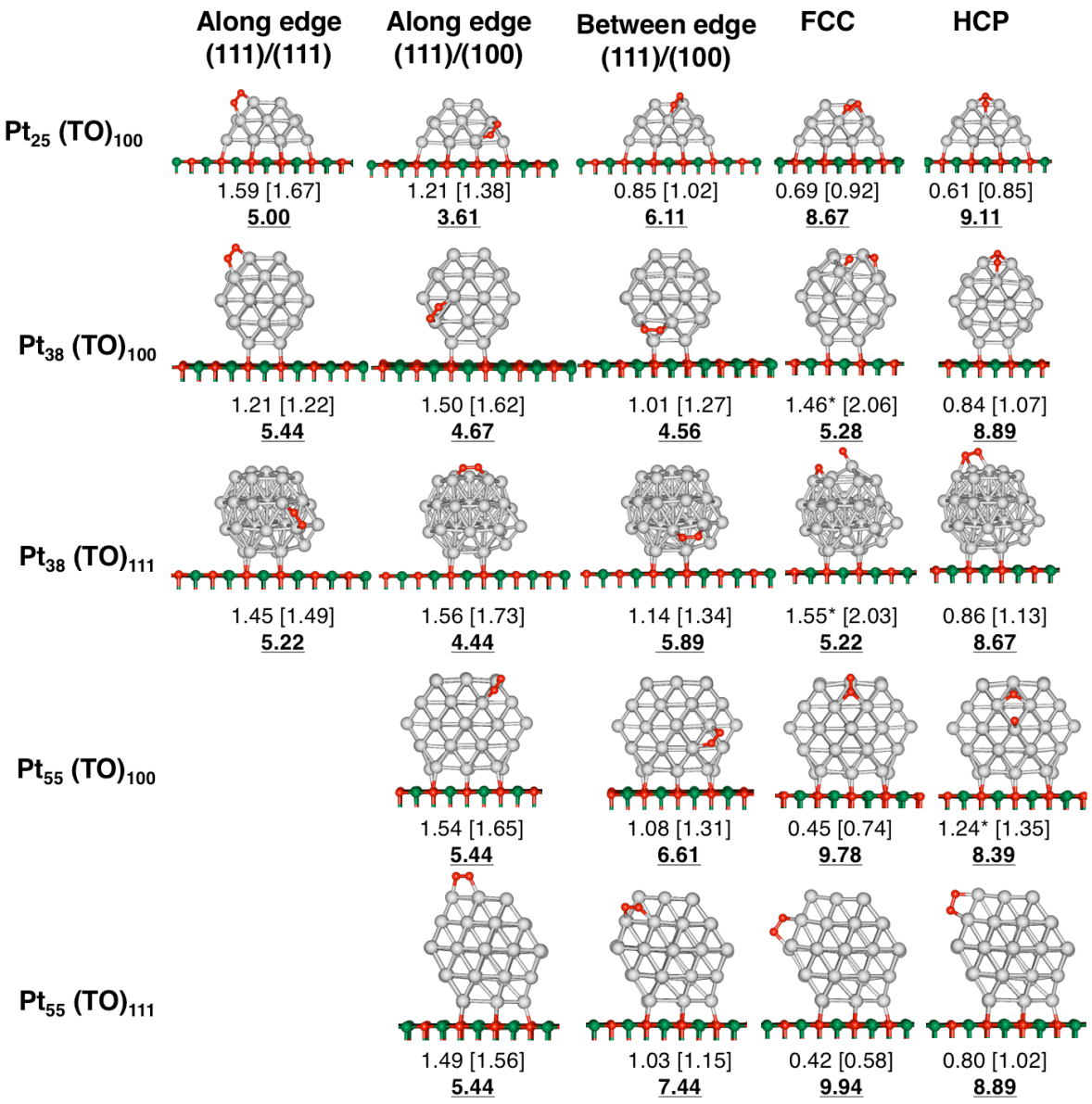

Fig. S1. O_2 adsorption sites considered for supported Pt clusters in the size range 25 - 55 atoms, involving truncated octahedral (TO) and cuboctahedral (CO) geometries. A distinction is made if the cluster is in contact with the substrate via one of its (100) or (111) facets. Calculated E_{ads} values are displayed in eV, while dispersion corrected (DFT-D) values are shown in brackets. An asterisk (*) indicated those configurations where O_2 spontaneous dissociated occurred during DFT relaxations. The corresponding GCN value at the adsorption site is provided in bold. Colour labelling: light grey (Pt), green (Mg) and red (O).

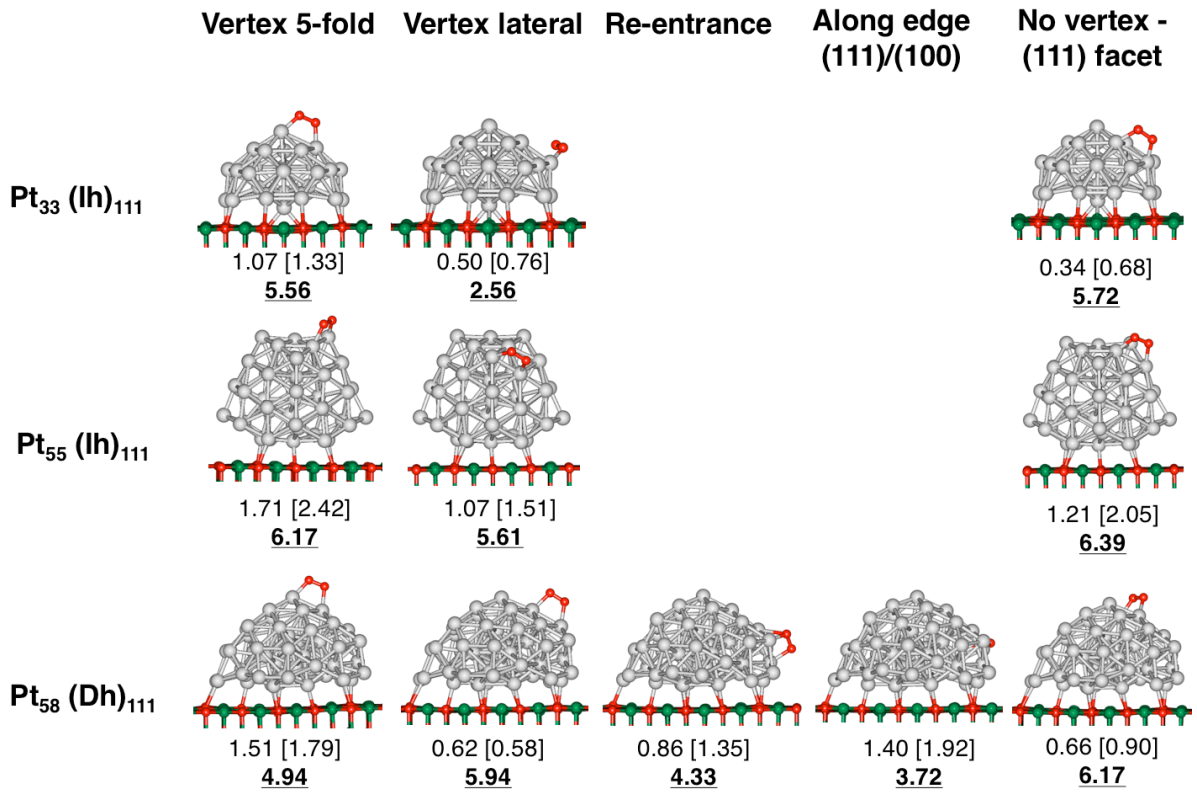

Fig. S2. O_2 adsorption sites considered for supported Pt clusters in the size range 33 - 58 atoms, involving icosahedral (Ih) and decahedral (Dh) geometries. The cluster/oxide interface involves the supported clusters (111) facets The corresponding GCN value at the adsorption site is provided in bold. Colour labelling: light grey (Pt), green (Mg) and red (O).

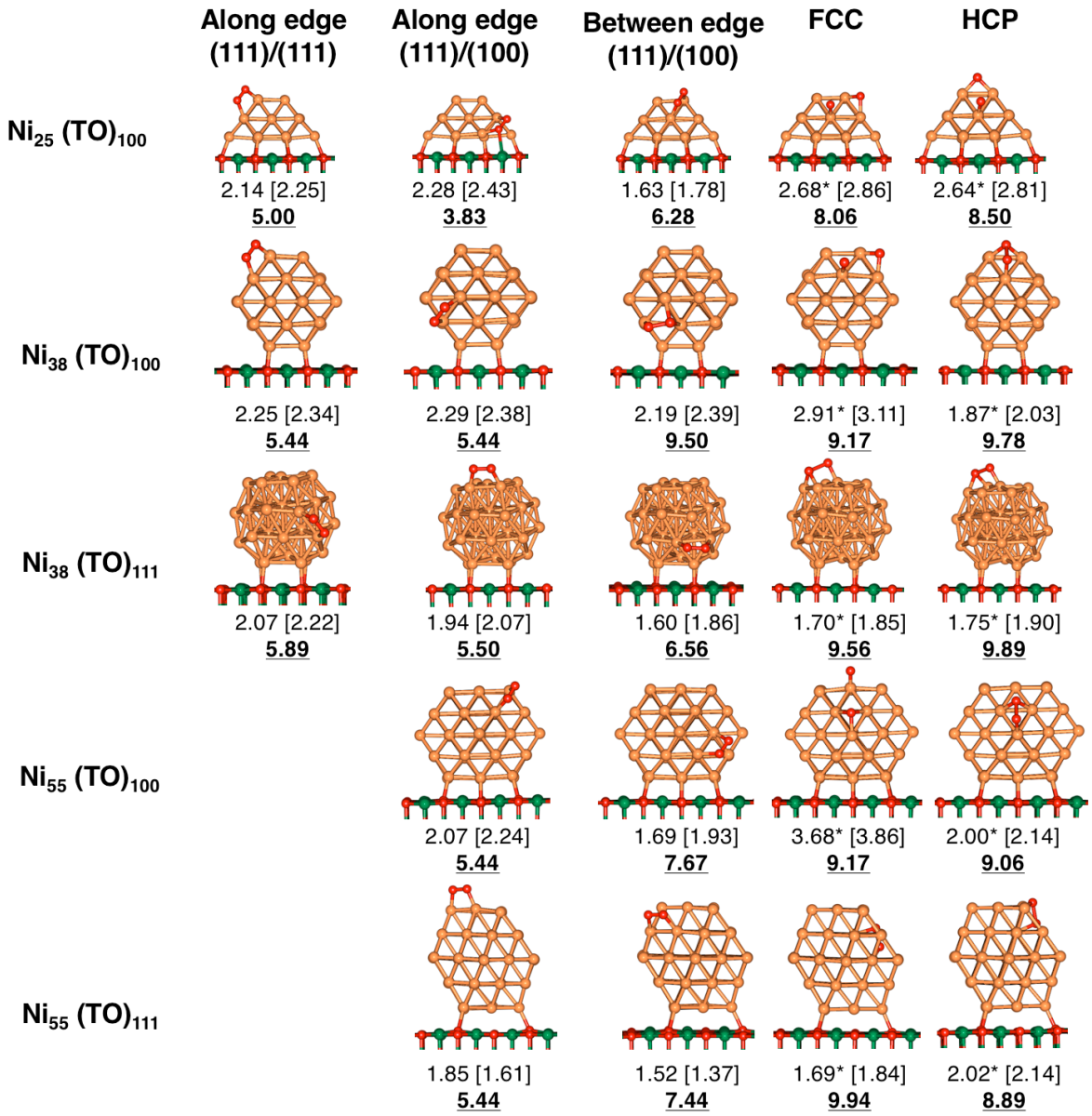

Fig. S3. O_2 adsorption sites considered for supported Pt clusters in the size range 25 - 55 atoms, involving truncated octahedral (TO) and cuboctahedral (CO) geometries. A distinction is made if the cluster is in contact with the substrate via one of its (100) or (111) facets. Calculated E_{ads} values are displayed in eV, while dispersion corrected (DFT-D) values are shown in brackets. An asterisk (*) indicated those configurations where O_2 spontaneous dissociated occurred during DFT relaxations. The corresponding GCN value at the adsorption site is provided in bold. Colour labelling: orange (Ni), green (Mg) and red (O).

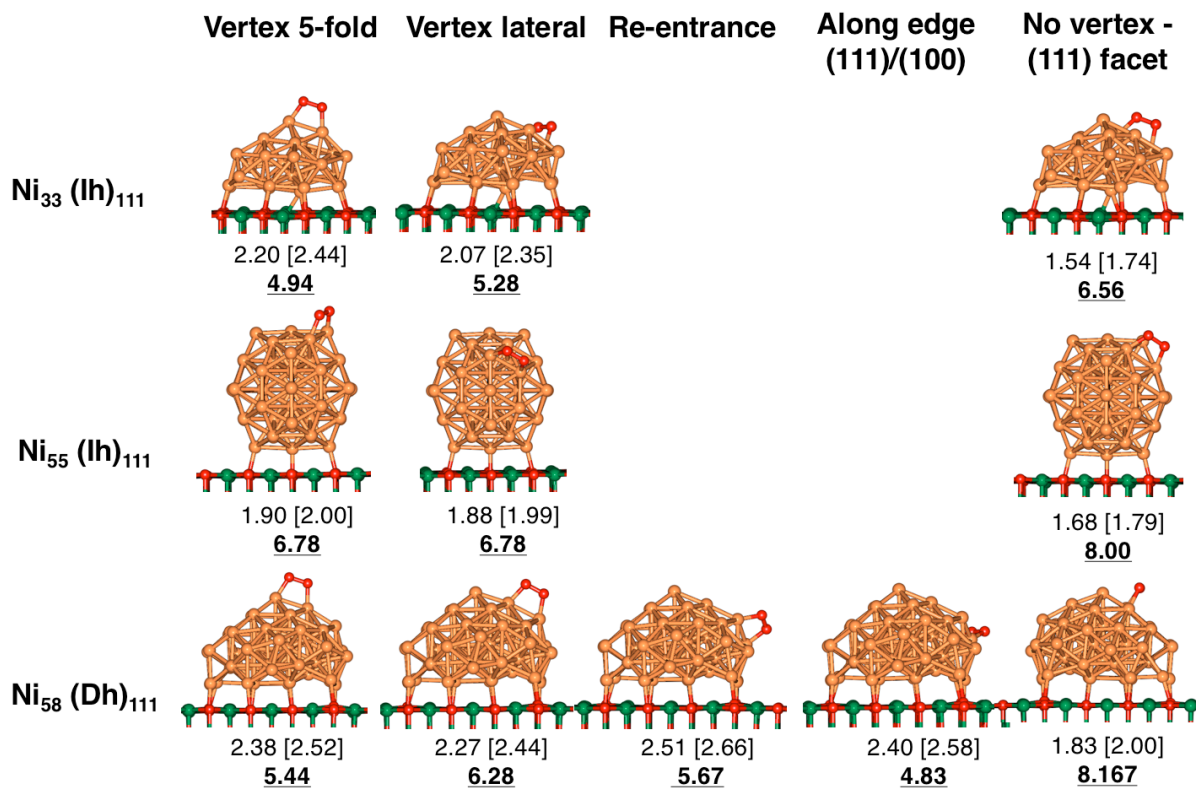

Fig. S4. O_2 adsorption sites considered for supported Pt clusters in the size range 33 - 58 atoms, involving icosahedral (Ih) and decahedral (Dh) geometries. The cluster/oxide interface involves the supported clusters (111) facets. The corresponding GCN value at the adsorption site is provided in bold. Colour labelling: orange (Ni), green (Mg) and red (O).

Tables

O_2 @ PtNi/ MgO(100)	O_2 adsorption site	Metal-Metal bond length at adsorption site (Å)	O-O Adsorbed molecule bond length (Å)	Cluster core strain (%)	Cluster shell strain (%)	Cluster interface roughness (std. dev.)	Number of metal atoms at interface	Cluster interface mean height (Å)	Cluster average bond length (Å)	GCN value	PBE E_{ads} (eV)	DFT+D E_{ads} (eV)
$Pt_{20}Ni_5$ TO (100)	*Along edge (111)/(111)*	2.598	1.420	-3.695	-3.393	0.033	12	2.223	2.664	5.000	1.270	1.470
	Along edge (111)/(100)	2.618	1.448	-3.772	-3.322	0.125	12	2.268	2.677	3.833	1.410	1.600
	Between edge (111)/(100)	2.662	1.386	-4.721	-2.998	0.055	12	2.233	2.670	6.111	0.990	1.370
	FCC	2.856	1.848	-3.903	-3.082	0.040	12	2.211	2.675	8.667	0.640	0.930
	HCP	2.818	2.950	-4.146	-2.531	0.028	12	2.221	2.690	8.500	0.900	1.190
$Pt_{21}Ni_{12}$ Ih (111)	*Vertex 5-fold*	3.391	1.405	-6.271	-4.272	0.240	13	2.242	2.659	6.556	1.860	2.960
	Vertex lateral	2.533	1.401	-10.032	-3.689	0.192	12	2.232	2.681	4.722	1.690	2.440
	No vertex - (111) facet	2.961	1.374	-7.747	-3.352	0.245	13	2.289	2.631	7.944	1.430	2.270
$Pt_{32}Ni_6$ TO (100)	*Along edge (111)/(111)*	2.933	1.409	-9.010	-1.127	0.014	4	2.116	2.895	4.444	1.940	1.930
	Along edge (111)/(100)	3.012	1.405	-7.983	-1.728	0.033	4	2.137	2.862	5.333	1.710	1.780
	Between edge (111)/(100)	2.639	1.382	-9.281	-1.438	0.027	4	2.109	2.867	9.000	1.110	1.120
	FCC	2.839	1.810	-8.438	-1.686	0.005	4	2.099	2.867	9.389	0.110	0.230
	HCP	2.733	1.417	-8.837	-1.860	0.013	4	2.092	2.880	9.500	0.640	0.880
$Pt_{32}Ni_6$ TO (111)	*Along edge (111)/(111)*	3.214	1.396	-9.282	-1.201	0.159	7	2.216	2.749	4.167	1.690	1.900
	Along edge (111)/(100)	3.092	1.394	-9.146	-1.471	0.101	7	2.183	2.781	4.611	1.570	2.010
	Between edge (111)/(100)	2.833	1.384	-8.810	-1.251	0.081	7	2.178	2.790	6.278	1.530	1.240
	FCC	2.823	1.431	-10.487	-1.042	0.170	7	2.279	2.785	6.722	0.180	0.310
	HCP	2.715	1.422	-10.544	-0.993	0.168	7	2.274	2.776	7.611	0.410	0.590
$Pt_{42}Ni_{13}$ CO (100)	*Along edge (111)/(100)*	2.690	1.405	-6.823	-2.903	0.113	9	2.199	2.721	5.444	0.770	0.910
	Between edge (111)/(100)	2.677	1.382	-7.272	-2.786	0.107	9	2.206	2.735	7.333	0.750	0.990
	FCC	2.609	1.820	-6.870	-2.882	0.112	9	2.205	2.721	9.056	0.370	0.550
	HCP	2.831	1.417	-6.829	-2.778	0.118	9	2.208	2.723	9.778	0.390	0.660
$Pt_{42}Ni_{13}$ CO (111)	*Along edge (111)/(100)*	2.921	1.407	-7.695	-2.112	0.054	6	2.189	2.786	4.667	1.580	1.810
	Between edge (111)/(100)	2.667	1.376	-7.931	-2.222	0.053	6	2.186	2.784	7.444	1.080	1.150
	FCC	2.840	1.411	-7.886	-2.613	0.073	6	2.188	2.760	9.778	0.310	0.590
	HCP	2.747	2.466	-7.835	-2.661	0.069	6	2.192	2.763	8.667	0.580	0.800
$Pt_{42}Ni_{13}$ Ih (111)	*Vertex 5-fold*	2.752	1.388	-7.851	-0.897	0.067	6	2.240	2.814	6.778	0.960	1.090
	Vertex lateral	2.756	1.386	-7.898	-0.909	0.062	6	2.238	2.812	6.778	0.910	1.070
	No vertex - (111) facet	2.933	1.395	-7.937	-0.802	0.053	6	2.257	2.828	6.778	0.560	0.750
$Pt_{47}Ni_{11}$ Dh (111)	*Vertex 5-fold*	2.750	1.379	-4.949	-1.685	0.108	15	2.246	2.836	6.889	1.090	1.740
	Vertex lateral	2.729	1.387	-4.996	-2.204	0.127	15	2.259	2.785	6.222	1.500	1.740
	Reentrance	2.700	1.405	-5.871	-2.019	0.106	15	2.248	2.786	5.056	1.640	1.910
	Along edge (111)/(100)	2.680	1.400	-4.821	-1.597	0.158	15	2.260	2.763	5.000	1.970	2.140
	No vertex - (111) facet	2.770	1.381	-4.791	-1.607	0.224	16	2.316	2.773	7.278	1.400	1.540

Table S1. Structural properties of supported PtNi clusters upon molecular O_2 adsorption at all the different inequivalent sites considered in this work.

O_2 @ Pt / MgO(100)	O_2 adsorption site	Metal-Metal bond length at adsorption site (Å)	O-O Adsorbed molecule bond length (Å)	Cluster core strain (%)	Cluster shell strain (%)	Cluster interface roughness (std. dev.)	Number of metal atoms at interface	Cluster interface mean height (Å)	Cluster average bond length (Å)	GCN value	PBE E_{ads} (eV)	DFT+D E_{ads} (eV)
Pt_{25} TO (100)	*Along edge (111)/(111)*	2.623	1.408	-6.045	-4.623	0.071	12	2.201	2.682	5.000	1.590	1.670
	Along edge (111)/(100)	2.670	1.432	-5.222	-4.912	0.111	12	2.210	2.680	3.611	1.210	1.380
	Between edge (111)/(100)	2.699	1.405	-5.618	-4.417	0.060	12	2.204	2.680	6.111	0.850	1.020
	FCC	2.786	1.434	-5.875	-4.573	0.067	12	2.163	2.683	8.667	0.690	0.920
	HCP	2.780	1.430	-6.107	-4.480	0.069	12	2.163	2.684	9.111	0.610	0.850
Pt_{33} Ih (111)	*Vertex 5-fold*	3.102	1.416	-3.719	-4.265	0.295	14	2.337	2.721	5.556	1.070	1.330
	Vertex lateral	*1 Pt atom only*	1.309	-4.048	-4.342	0.281	14	2.336	2.716	2.556	0.500	0.760
	No vertex - (111) facet	2.995	1.386	-4.769	-4.045	0.285	14	2.329	2.725	5.722	0.340	0.680
Pt_{38} TO(100)	*Along edge (111)/(111)*	2.617	1.426	-4.644	-3.963	0.027	4	2.123	2.844	5.444	1.210	1.220
	Along edge (111)/(100)	3.170	1.398	-4.618	-4.045	0.017	4	2.111	2.838	4.667	1.500	1.620
	Between edge (111)/(100)	2.872	1.426	-5.124	-4.071	0.030	4	2.150	2.851	4.556	1.010	1.270
	FCC	2.878	3.002	-5.461	-4.105	0.009	4	2.101	2.823	5.278	1.460	2.060
	HCP	2.796	1.431	-5.164	-4.041	0.011	4	2.094	2.835	8.889	0.840	1.070
Pt_{38} TO(111)	*Along edge (111)/(111)*	2.689	1.407	-4.289	-3.667	0.256	7	2.330	2.777	5.222	1.450	1.490
	Along edge (111)/(100)	3.334	1.396	-5.042	-3.687	0.227	6	2.280	2.785	4.444	1.560	1.730
	Between edge (111)/(100)	2.741	1.419	-4.511	-4.174	0.279	7	2.337	2.724	5.889	1.140	1.340
	FCC	2.773	2.923	-5.643	-3.744	0.249	6	2.248	2.765	5.222	1.550	2.030
	HCP	2.782	1.418	-5.379	-3.678	0.232	6	2.250	2.754	8.667	0.860	1.130
Pt_{55} CO (100)	*Along edge (111)/(100)*	2.715	1.402	-3.239	-2.980	0.088	9	2.150	2.782	5.444	1.540	1.650
	Between edge (111)/(100)	2.908	1.382	-3.253	-2.901	0.080	9	2.137	2.770	6.611	1.080	1.310
	FCC	2.985	1.409	-2.849	-3.108	0.085	9	2.140	2.776	9.778	0.450	0.740
	HCP	2.925	3.043	-3.039	-2.874	0.083	9	2.148	2.786	8.389	1.240	1.350
Pt_{55} CO (111)	*Along edge (111)/(100)*	2.726	1.402	-3.597	-3.411	0.050	6	2.125	2.833	5.444	1.490	1.560
	Between edge (111)/(100)	2.954	1.378	-3.790	-3.606	0.035	6	2.117	2.805	7.444	1.030	1.150
	FCC	3.038	1.431	-3.617	-3.572	0.053	6	2.097	2.825	9.944	0.420	0.580
	HCP	2.757	1.448	-3.729	-3.463	0.049	6	2.096	2.828	8.889	0.800	1.020
Pt_{55} Ih(111)	*Vertex 5-fold*	2.767	1.401	-4.785	-3.999	0.138	7	2.262	2.780	6.167	1.710	2.420
	Vertex lateral	2.667	1.384	-4.606	-3.834	0.136	7	2.277	2.807	5.611	1.070	1.510
	No vertex - (111) facet	2.821	1.403	-4.817	-4.123	0.141	7	2.259	2.777	6.389	1.210	2.050
Pt_{58} Dh(111)	*Vertex 5-fold*	2.677	1.385	-1.579	-3.547	0.253	14	2.357	2.754	4.944	1.510	1.790
	Vertex lateral	2.659	1.375	-0.744	-3.823	0.226	14	2.347	2.754	5.944	0.620	0.580
	Reentrance	2.784	1.406	-1.563	-3.879	0.183	11	2.251	2.730	4.333	0.860	1.350
	Along edge (111)/(100)	*1 Pt atom only*	1.386	-2.019	-3.874	0.257	12	2.301	2.780	3.722	1.400	1.920
	No vertex - (111) facet	2.719	1.378	-0.965	-3.867	0.236	14	2.345	2.754	6.167	0.660	0.900

Table S2. Structural properties of supported Pt clusters upon molecular O_2 adsorption at all the different inequivalent sites considered in this work.

O_2 @ Ni / MgO(100)	O_2 adsorption site	Metal-Metal bond length at adsorption site (Å)	O-O Adsorbed molecule bond length (Å)	Cluster core strain (%)	Cluster shell strain (%)	Cluster interface roughness (std. dev.)	Number of metal atoms at interface	Cluster interface mean height (Å)	Cluster average bond length (Å)	GCN value	PBE E_{ads} (eV)	DFT+D E_{ads} (eV)
Ni_{25} TO (100)	*Along edge (111)/(111)*	2.469	1.416	3.162	-3.092	0.094	12	1.913	2.515	5.000	2.140	2.250
	Along edge (111)/(100)	2.424	1.461	3.100	-3.290	0.109	12	1.947	2.524	3.833	2.280	2.430
	Between edge (111)/(100)	2.508	1.432	2.774	-3.111	0.086	12	1.917	2.523	6.278	1.630	1.780
	FCC	2.514	3.085	3.101	-2.754	0.088	12	1.912	2.523	8.056	2.680	2.860
	HCP	2.517	3.254	3.590	-2.795	0.090	12	1.915	2.518	8.500	2.640	2.810
Ni_{33} Ih (111)	*Vertex 5-fold*	2.538	1.418	-0.712	-1.132	0.320	14	2.152	2.569	4.944	2.200	2.200
	Vertex lateral	2.625	1.418	0.847	-1.352	0.296	14	2.164	2.564	5.278	2.070	2.350
	No vertex - (111) facet	2.442	1.424	1.514	-1.603	0.301	14	2.167	2.567	6.556	1.540	1.740
Ni_{38} TO (111)	*Along edge (111)/(111)*	2.455	1.415	-2.219	-1.090	0.314	7	2.313	2.473	5.889	2.070	2.340
	Along edge (111)/(100)	2.474	1.410	-2.081	-1.073	0.321	7	2.316	2.476	5.500	1.940	2.380
	Between edge (111)/(100)	2.688	1.454	-2.431	-0.904	0.318	7	2.318	2.512	6.556	1.600	2.390
	FCC	2.616	1.754	-2.384	-0.825	0.311	7	2.310	2.473	9.556	1.700	3.110
	HCP	2.578	1.731	-2.369	-1.069	0.313	7	2.310	2.467	9.889	1.750	2.030
Ni_{38} TO (100)	*Along edge (111)/(111)*	2.486	1.411	-1.474	-2.796	0.011	4	1.883	2.597	5.444	2.250	2.220
	Along edge (111)/(100)	2.426	1.425	-1.675	-2.757	0.012	4	1.906	2.600	5.444	2.290	2.070
	Between edge (111)/(100)	2.539	1.577	-1.472	-2.902	0.009	4	1.900	2.569	9.500	2.190	1.860
	FCC	2.539	3.243	-1.388	-2.791	0.008	4	1.865	2.580	9.167	2.910	1.850
	HCP	2.545	1.751	-1.746	-2.800	0.009	4	1.873	2.588	9.778	1.870	1.900
Ni_{55} CO(111)	*Along edge (111)/(100)*	2.401	1.420	-1.514	-1.955	0.055	6	2.233	2.588	5.444	1.850	2.240
	Between edge (111)/(100)	2.523	1.415	-1.525	-2.058	0.053	6	2.213	2.578	7.444	1.520	1.930
	FCC	2.552	1.701	-1.435	-2.077	0.029	6	2.040	2.608	9.944	1.690	3.860
	HCP	2.583	1.750	-1.479	-2.040	0.030	6	2.038	2.612	8.889	2.020	2.140
Ni_{55} CO(100)	*Between edge (111)/(100)*	2.482	1.435	-1.356	-1.750	0.072	9	1.982	2.599	7.667	1.690	1.610
	Along edge (111)/(100)	2.465	1.419	-1.365	-1.803	0.079	9	1.981	2.601	5.444	2.070	1.370
	FCC	2.730	3.654	-1.141	-1.730	0.077	9	1.993	2.600	9.167	3.680	1.840
	HCP	2.510	1.824	-1.216	-1.752	0.075	9	1.996	2.602	9.056	2.000	2.140
Ni_{55} Ih (111)	*Vertex 5-fold*	2.508	1.409	-1.685	0.044	0.387	7	2.356	2.572	6.778	1.900	2.000
	Vertex lateral	2.509	1.409	-1.689	0.049	0.387	7	2.352	2.573	6.778	1.880	1.990
	No vertex - (111) facet	2.590	1.435	-1.621	0.038	0.387	7	2.355	2.573	8.000	1.680	1.790
Ni_{58} Dh (111)	*Vertex 5-fold*	2.428	1.416	-0.369	-0.933	0.196	14	2.036	2.552	5.444	2.380	2.520
	Vertex lateral	2.430	1.413	-0.500	-0.933	0.188	14	2.036	2.547	6.278	2.270	2.440
	Reentrance	2.577	1.414	-0.488	-1.068	0.184	14	2.033	2.542	5.667	2.510	2.660
	Along edge (111)/(100)	2.457	1.414	-0.580	-1.156	0.182	14	2.038	2.548	4.833	2.400	2.580
	No vertex - (111) facet	2.609	1.428	-0.363	-0.914	0.198	14	2.034	2.549	8.167	1.830	2.000

Table S3. Structural properties of supported Ni clusters upon molecular O_2 adsorption at all the different inequivalent sites considered in this work.

Composition	Structure	O_2 adsorption sites	
		Strongest **site in eV**	***Weakest*** **site in eV**
$Pt_{20}Ni_5$	TO (100)	-3.781	-3.252*
$Pt_{21}Ni_{12}$	Ih(111)	-3.478	-2.783
$Pt_{32}Ni_6$	TO (100)	-3.841	-4.039*
$Pt_{32}Ni_6$	TO (111)	-3.437	-3.626
$Pt_{42}Ni_{13}$	CO (100)	-2.972	-2.854*
$Pt_{42}Ni_{13}$	CO (111)	-2.949	-2.671
$Pt_{42}Ni_{13}$	Ih (111)	-3.472	-3.239
$Pt_{47}Ni_{11}$	Dh (111)	-2.795	-2.687

Table S4. Calculated average *d*-band center of supported PtNi clusters on MgO(100) upon O_2 adsorption. The asterisk (*) highlight those configurations involving a dissociated O_2 molecule.