Supporting Information

Adsorption of CO on Low-Energy, Low-Symmetry Pt Nanoparticles: Energy Decomposition Analysis and Prediction via Machine-Learning Models

Raymond Gasper, [(1),†] Hongbo Shi,[(1),†] and Ashwin Ramasubramaniam[(2),*]

(1) Department of Chemical Engineering, University of Massachusetts, Amherst MA 01003, USA

(2) Department of Mechanical and Industrial Engineering, University of Massachusetts, Amherst MA 01003, USA

† These authors contributed equally to this work

* Corresponding Author: ashwin@engin.umass.edu; Phone: +1-413-545-4866

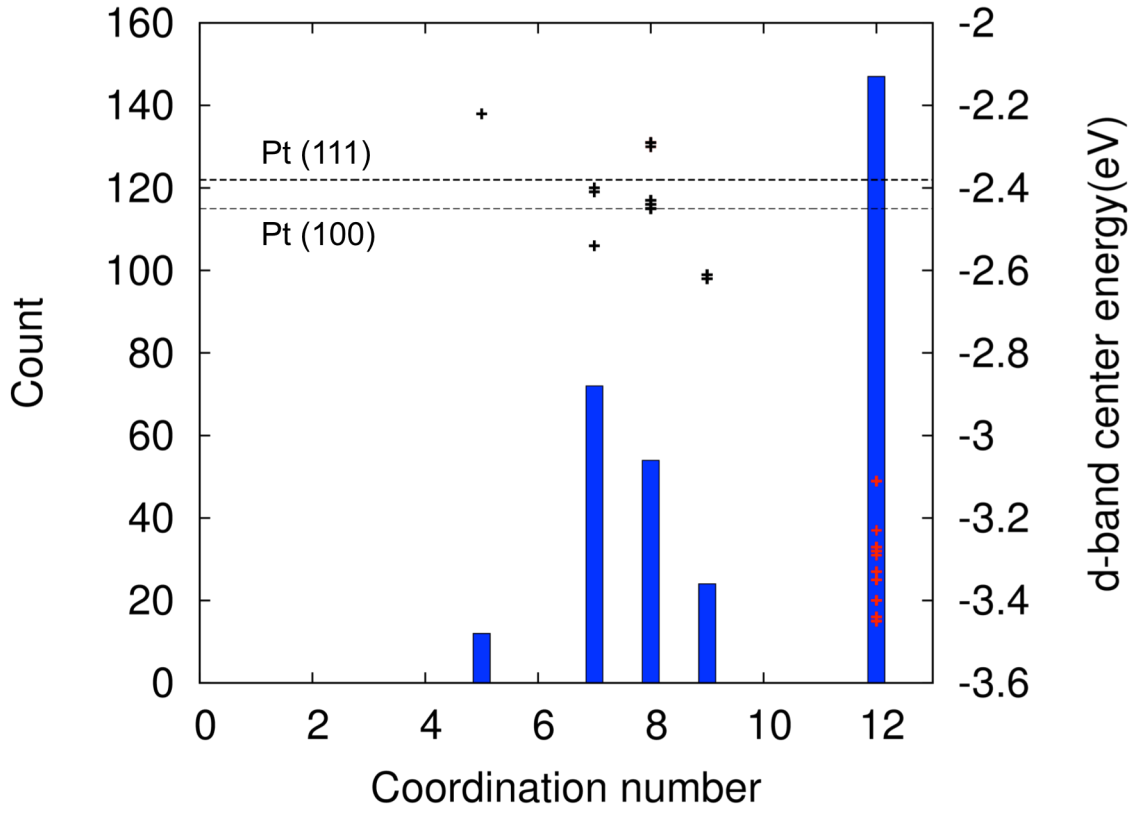

Figure S1: Distribution of coordination numbers (blue bars) as well as *d*-band center energies of atoms on the surface (black "+" symbols) and in the bulk (red "+" symbols) for the cuboctahedral Pt_{309} cluster. Surface *d*-band centers of FCC Pt(111) and Pt(100) surfaces are shown for reference.

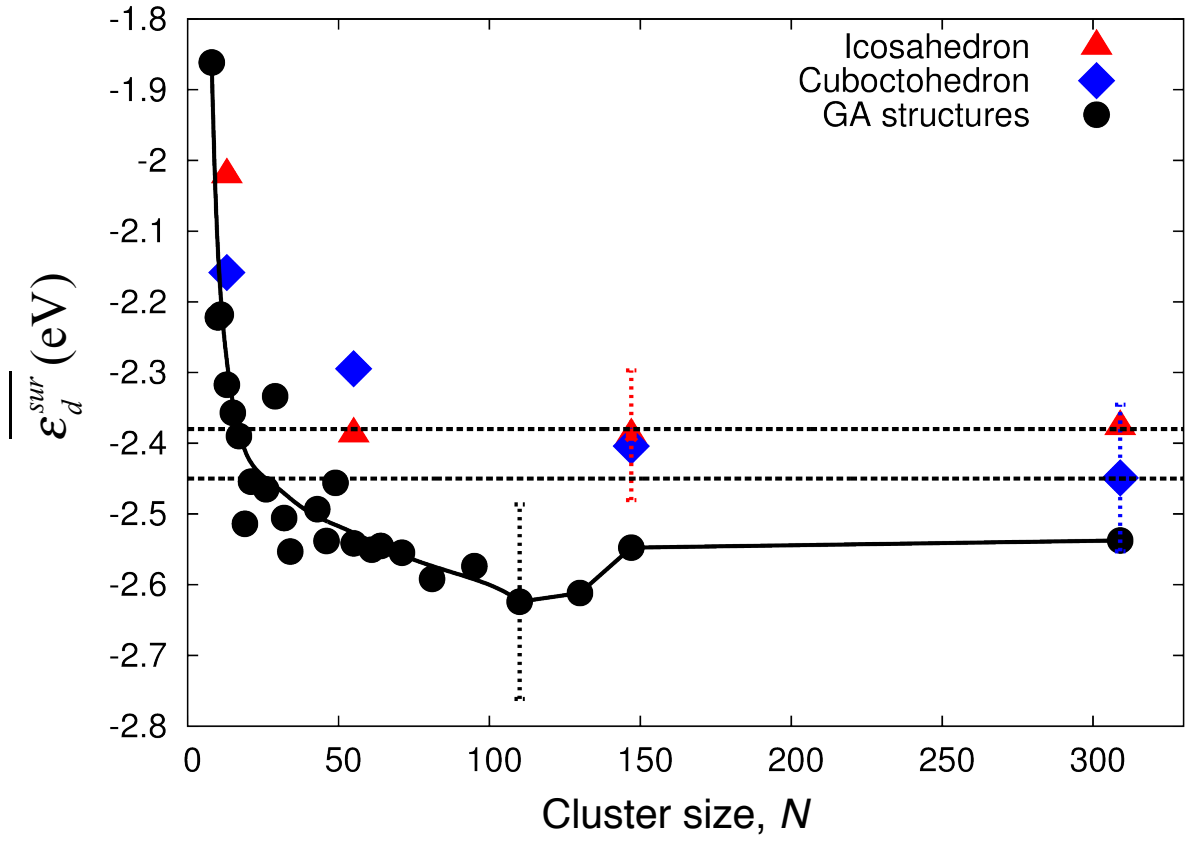

Figure S2: Average *d*-band center energy of the surface atoms, $\overline{\varepsilon_d^{sur}}$, as a function of cluster size, *N*. The solid curve passing through data for GA-optimized structures is merely a guide to the eye. Error bars are standard deviations; representative error bars are shown only for certain sizes to maintain legibility. The exact values of *d*-band center energy with confidence intervals for every data point can be found in Table S1. Horizontal dashed lines indicate the reference *d*-band center energies on bulk-terminated, FCC Pt(111) and (100) surfaces.

Table S1: Average *d*-band center energy of surface atoms, $\overline{\varepsilon_d^{sur}}$, and standard deviations, σ, as a function of cluster size, *N*.

	GA-optimized		**Icosahedron**		**Cuboctahedron**	
N	$\overline{\varepsilon_d^{sur}}$	σ	$\overline{\varepsilon_d^{sur}}$	σ	$\overline{\varepsilon_d^{sur}}$	σ
8	-1.86	0.14				
10	-2.22	0.38				
11	-2.22	0.36				
13	-2.32	0.27	-2.02	0.09	-2.16	–
15	-2.36	0.17				
17	-2.39	0.27				
19	-2.51	0.26				
21	-2.45	0.13				
26	-2.46	0.22				
29	-2.33	0.24				
32	-2.51	0.19				
34	-2.55	0.21				
43	-2.49	0.17				
46	-2.54	0.15				
49	-2.46	0.13				
55	-2.54	0.21	-2.39	0.11	-2.29	0.08
61	-2.55	0.15				
64	-2.55	0.13				
71	-2.55	0.11				
81	-2.59	0.16				
95	-2.57	0.15				
110	-2.62	0.14				
130	-2.61	0.17				
147	-2.55	0.15	-2.39	0.09	-2.40	0.08
309	-2.54	0.10	-2.38	0.10	-2.45	0.10

Table S2: Average all-relaxed ($\overline{E_{ads}^{AR}}$), frozen cluster ($\overline{E_{ads}^{FC}}$), and all-frozen ($\overline{E_{ads}^{AF}}$) CO adsorption energies and Student-T corrected errors (95% confidence intervals) as a function of cluster size on Pt_N clusters; for the 4-atom cluster the reported errors are standard deviations.

	$\overline{E_{ads}^{AR}}$		$\overline{E_{ads}^{FC}}$		$\overline{E_{ads}^{AF}}$	
N	Avg.	Err.	Avg.	Err.	Avg.	Err.
4	-2.86	0.29	-2.69	0.31	–	–
8	-3.19	–	-2.74	–	-2.70	–
13	-2.33	0.22	-1.96	0.34	-1.93	0.20
34	-2.21	0.06	-1.96	0.11	-1.95	0.08
43	-2.05	0.14	-1.68	0.20	-1.56	0.19
46	-1.95	0.11	-1.68	0.19	-1.54	0.27
55	-1.78	0.13	-1.57	0.17	-1.40	0.15
61	-1.89	0.15	-1.61	0.27	-1.47	0.30
64	-1.98	0.20	-1.66	0.26	-1.59	0.29
71	-2.09	0.09	-1.67	0.15	-1.56	0.13
81	-2.19	0.18	-1.77	0.22	-1.67	0.23
110	-1.89	0.16	-1.54	0.14	-1.48	0.12
147	-1.98	0.13	-1.63	0.22	-1.59	0.22

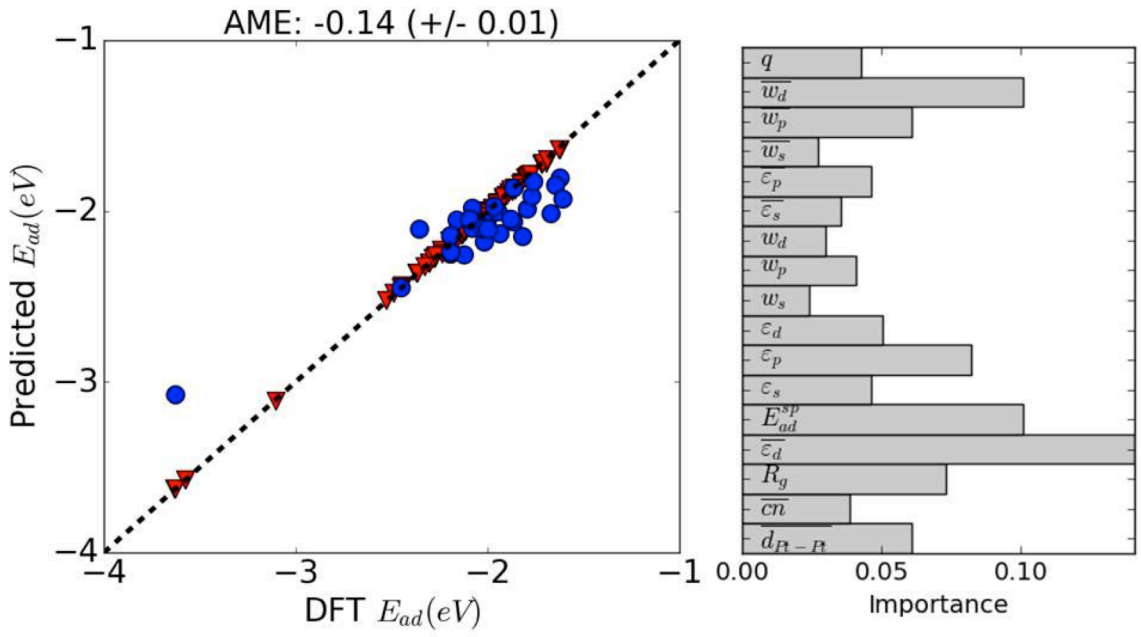

Figure S3: DFT-calculated CO adsorption energies on the surface sites of Pt clusters versus the prediction from GBR model with all descriptors. Below is a list of the descriptors used for this figure:

q valence electrons associated with each atom (from Bader analysis)
$\overline{w_d}$ general *d*-band width
$\overline{w_p}$ general *p*-band width
$\overline{w_s}$ general *s*-band width
w_d *d*-band width
w_p *p*-band width
w_s *s*-band width
$\overline{\varepsilon_d}$ general *d*-band center energy with respect to the Fermi level
$\overline{\varepsilon_p}$ general *p*-band center energy with respect to the Fermi level
$\overline{\varepsilon_s}$ general *s*-band center energy with respect to the Fermi level
ε_d *d*-band center energy with respect to the Fermi level
ε_p *p*-band center energy with respect to the Fermi level
ε_s *s*-band center energy with respect to the Fermi level

The remaining descriptors are explained in Section 3.3 of the paper.