

Electronic Supplementary Information

Can the state of platinum species be unambiguously determined by the stretching frequency of adsorbed CO probe molecule?

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Table S1.

Energetic (in eV) and structural (in pm) characteristics of the modeled Pt₈CO complexes in gas phase.

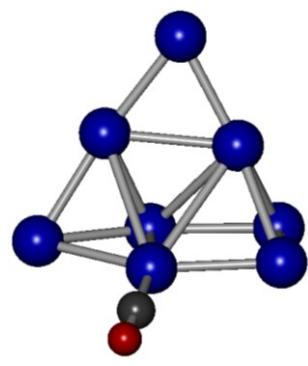
Structure	C ^a	Ns	E _{rel} ^b	CN	BE	R(Pt-C)	ΔR(C-O) ^c	v(C-O) ^d
Pt ₈ CO_a	t	2	0.00	5	2.73	184	2.2	2041
Pt ₈ CO_b	t	2	0.10	3	2.62	183	2.4	2024
Pt ₈ CO_c	t	2	0.34	5	2.38	183	2.2	2039
Pt ₈ CO_d	b	0	0.34		2.38	201, 201	4.3	1850
Pt ₈ CO_e	b	2	0.34	2-5	2.39	193, 203	4.7	1849
Pt ₈ CO_f	b	4	0.49		2.25	195, 201	4.4	1862
Pt ₈ CO_g	b	0	0.56	3-5	2.18	194, 204	4.9	1827
Pt ₈ CO_h	t	0	0.60	5	2.12	183	2.1	2040
Pt ₈ CO_i	b	4	0.62		2.10	195, 199	5.2	1798
Pt ₈ CO_j	b	4	0.66		2.07	195, 195	5.2	1796
Pt ₈ CO_k	b	4	0.75	3-5	1.98	197, 197	4.8	1827
Pt ₈ CO_l	t	4	0.76	3	1.97	187	2.0	2029
Pt ₈ CO_m	h	4	0.77		1.96	203, 203, 215	6.2	1724
Pt ₈ CO_n	b	2	0.81		1.92	193, 205	4.5	1852
Pt ₈ CO_o	t	2	0.82	2	1.92	186	2.2	2019
Pt ₈ CO_p	h	4	0.91		1.81	203, 203, 207	6.5	1720
Pt ₈ CO_q	h	4	1.01		1.73	204, 208, 216	5.6	1757

^a Coordination of the CO molecule to the Pt₈ cluster: top (t), bridge (b), three fold hollow (h)

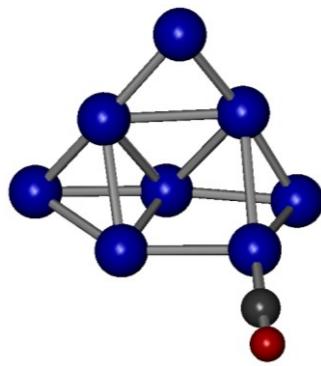
^b Relative energies with respect to the most stable structure

^c Δ(C-O) is the extension of C-O bond when it is coordinated to CO. The reference C-O distance is gas phase is 114.2 pm.

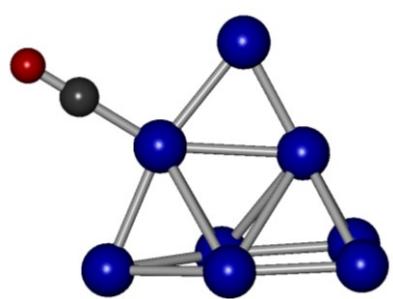
^d C-O vibrational frequencies are corrected by 14 cm⁻¹



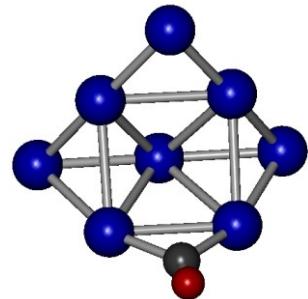
Pt_8CO_a



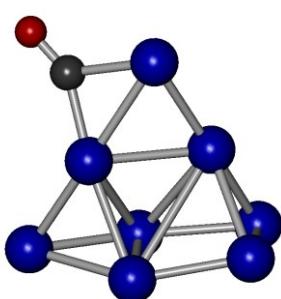
Pt_8CO_b



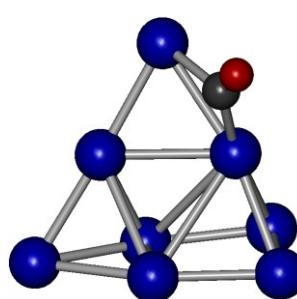
Pt_8CO_c



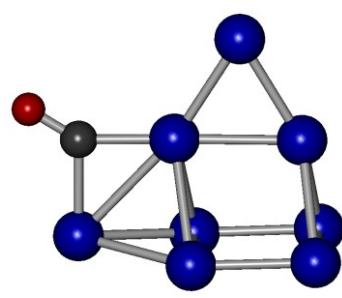
Pt_8CO_d



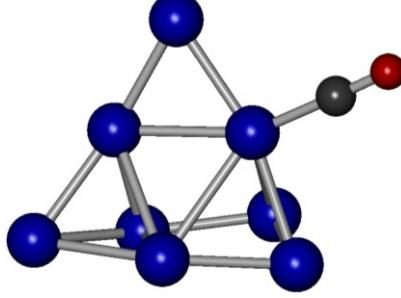
Pt_8CO_e



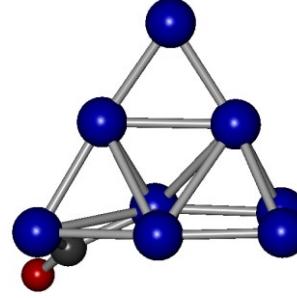
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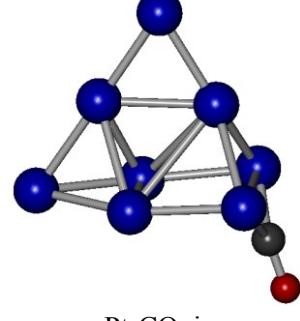
Pt_8CO_g



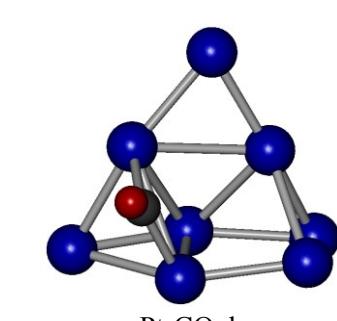
Pt_8CO_h



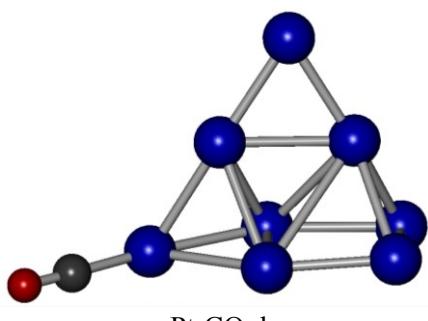
Pt_8CO_i



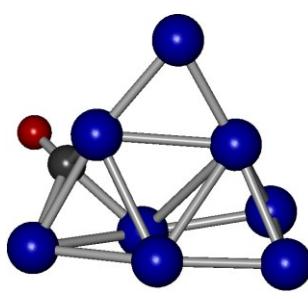
Pt_8CO_j



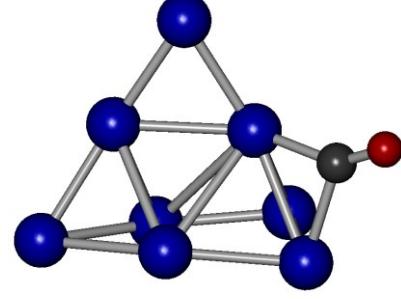
Pt_8CO_k



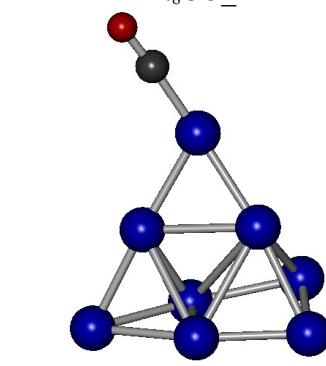
Pt_8CO_l



Pt_8CO_m



Pt_8CO_n



Pt_8CO_o

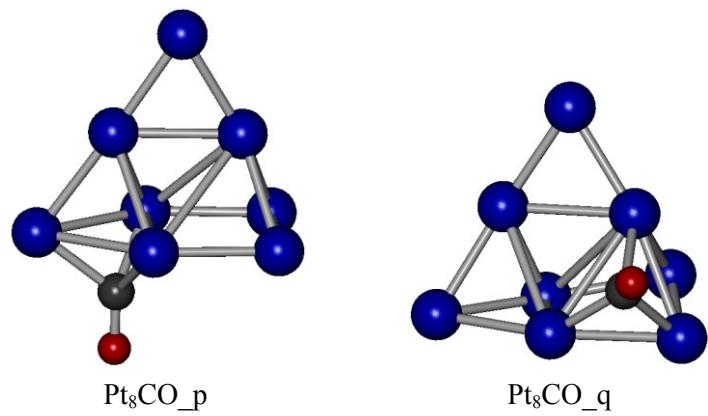


Figure S1

Optimized structures of the CO adsorbed on Pt₈ cluster in gas phase. Color coding: red – O; gray – C; dark blue – Pt. Cut-off for the Pt-Pt bonds is 330 pm.

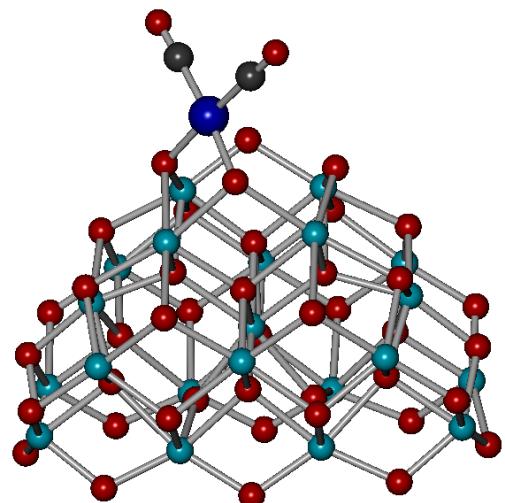


Figure S2

Optimized structure of the complex Pt(CO)₂/Ce₂₁O₄₂ in position e. Color coding: red – O; gray – C; light blue – Ce; dark blue – Pt.

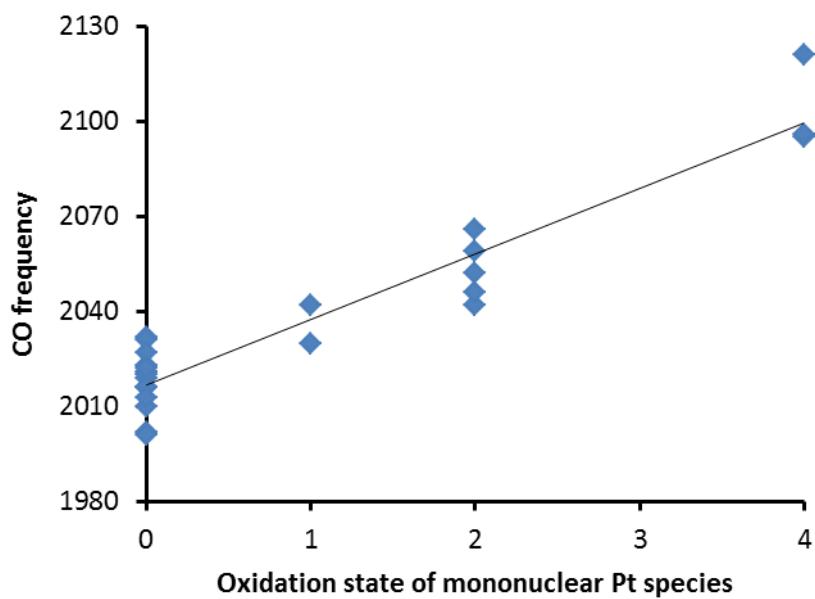


Figure S3. Calculated C-O vibrational frequency (in cm^{-1}) for CO coordinated on mononuclear platinum species on ceria nanoparticle versus the oxidation state of the platinum atom, n . The solid line shows the correlation $v = 2017 + 20.6 * n$ (RMSD = 0.90).

