Supplementary Material for PCCP

Supporting information

Table S1: Summary of calculated (GGA-PW91) properties of atomic O adsorption on Pt_x and Pt(111).

cluster	magnetic moment of system	O binding geometry	ZPE-corrected binding energy (eV)	d_{Pt-O} (Å)	ν_{Pt-O} (cm^{-1})	Bader charge of O (e)
Pt-O	2	-	-1.63	1.762	812	-0.48
Pt_2-O	2	apex	-1.41	1.766	855	-0.61
Pt_3-O	2	apex	-1.55	1.768	855	-0.65
Pt_4-O	2	apex	-1.73	1.772	860	-0.65
Pt_5-O	4	apex	-1.75	1.767	817	-0.65
Pt_{10}-O	4	apex	-1.07	1.774	869	-0.69
Pt(111)-O [a]	0	fcc	-1.09	2.058	432	-0.80

See Figure 1 for snapshots of the clusters. The free O atom has a magnetic moment of 2 in its ground state.

[a] $^1/_{16}$ ML coverage.

Table S2: Summary of calculated (GGA-PW91) properties of molecular oxygen (O_2) adsorption on Pt_x and Pt(111).

cluster	magnetic moment of system	O_2 binding geometry	ZPE-corrected binding energy (eV)	d_{O-O} (Å)	ν_{O-O} (cm^{-1})	Bader charge of O_2 (e)
O_2	2	-	-5.65 [a]	1.237	1571	-
Pt-O_2	2	bent	-1.62	1.294	1203	-0.34
Pt_2-O_2	2	η^2-O,O	-1.43	1.338	1126	-0.44
Pt_3-O_2	0	μ-O,O	-1.63	1.376	923	-0.58
Pt_4-O_2	0	μ-O,O	-2.44	1.409	793	-0.68
Pt_5-O_2	2	μ-O,O	-2.13	1.420	743	-0.67
Pt_{10}-O_2	4	μ-O,O	-1.33	1.425	729	-0.67
Pt(111)-O_2 [b]	0	top-bridge-top	-0.61	1.364	853	-0.60

The relevant properties of the free O_2 molecule are included for comparison. See Figure 1 for snapshots of the clusters.

[a] O_2 bond energy.

[b] $^1/_{16}$ ML coverage.

Table S3: Summary of calculated (GGA-PW91) properties of CO and NO adsorption on Pt_x clusters and Pt(111).

cluster	magnetic moment of system	CO/NO binding geometry	ZPE-corrected binding energy (eV)	∠ Pt-Y-O (º)	d_{Pt-Y} (Å)	d_{Y-O} (Å)	ν_{Y-O} (cm^{-1})	ν_{Pt-YO} (cm^{-1})	Bader charge of CO/NO (*e*)
CO	0	-	-10.70 [a]	-	-	1.144	2118	-	-
Pt-CO	0	linear	-3.46	180	1.772	1.165	2028	558	-0.06
Pt_2-CO	0	bridging	-2.95	138	1.915	1.192	1836	525	-0.28
Pt_3-CO	2	linear	-2.62	178	1.844	1.167	2019	527	-0.25
Pt_4-CO	2	linear	-2.62	176	1.843	1.167	1996	518	-0.23
Pt_5-CO	4	linear	-2.58	179	1.840	1.168	1992	519	-0.20
Pt_{10}-CO	6	linear	-2.01	179	1.830	1.166	2000	505	-0.20
Pt(111)-CO [b]	0	perp. atop	-1.65	180	1.862	1.157	2054	510	-0.15
NO	1	-	-6.37 [a]	-	-	1.175	1883	-	-
Pt-NO	1	bent	-3.19	132	1.816	1.189	1736	624	-0.24
Pt_2-NO	1	linear	-3.26	174	1.773	1.179	1875	578	-0.30
Pt_3-NO	1	linear	-3.10	178	1.773	1.182	1842	559	-0.36
Pt_4-NO	1	linear	-3.27	177	1.770	1.186	1833	595	-0.36
Pt_5-NO	3	linear	-3.04	176	1.783	1.183	1837	571	-0.29
Pt_{10}-NO	7	bent	-1.93	135	1.866	1.192	1724	580	-0.22
Pt(111)-NO [b]	0	perp. fcc	-1.89	-	2.083	1.215	1502	331	-0.50

The relevant properties of the free CO and NO molecules are included for comparison. "Y" = C or N. "perp." = perpendicular. See Figure 3 for snapshots of the clusters.

[a] CO/NO bond energy.

[b] $^1/_{16}$ ML coverage.

Table S4: Summary of calculated (GGA-PW91) properties of CO co-adsorbed with O_2, 2O, and O and CO_2 co-adsorbed with O on Pt_x (x = 1-5 and 10) and Pt(111).

cluster	magnetic moment of system	diff. $\nu_{C\text{-}O}$ (cm^{-1})	diff. $\nu_{Pt\text{-}CO}$ (cm^{-1})	diff. $\nu_{O\text{-}O}$/ $\nu_{Pt\text{-}O}$ (cm^{-1})	Bader charge diff. of CO (e)	Bader charge diff. of O/O_2/2O (e)
O_2-Pt-CO	2	35	3	48	-0.08	0.03
O_2-Pt_2-CO	0	44	-22	72	0.11	0.06
O_2-Pt_3-CO	0	6	1	356	0.03	0.20
O_2-Pt_4-CO	0	11	-10	-15	0.01	0.04
O_2-Pt_5-CO	2	20	18	-6	0.01	0.00
O_2-Pt_{10}-CO	4	9	43	91	0.05	0.03
Pt(111)-CO+O_2 [a]	0	-11	10	-6	0.13	0.04
2O-Pt-CO	2	49	-58		0.02	0.22
2O-Pt_2-CO	0	207	-20		0.13	0.09
2O-Pt_3-CO	0	8	-22		0.08	0.03
2O-Pt_4-CO	0	44	9		0.10	-0.07
2O-Pt_5-CO	2	49	-11		0.12	0.00
2O-Pt_{10}-CO	2	17	20		0.07	-0.03
Pt(111)-CO+2O [b]	0	-11	-20		0.03	-0.01
O-Pt-CO	2	16	-76	-125	-0.04	-0.01
O-Pt_2-CO	2	194	29	-204	0.10	-0.04
O-Pt_3-CO	2	15	-2	-48	0.05	0.03
O-Pt_4-CO	2	37	0	-17	0.05	0.03
O-Pt_5-CO	2	7	-6	53	0.05	0.04
O-Pt_{10}-CO	2	18	20	-40	0.01	0.01
Pt(111)-CO+O [a]	0	-7	-43	85	0.05	0.05

cluster	magnetic moment of system	diff. ν_{asOCO} (cm^{-1})	diff. $\nu_{Pt\text{-}O}$ (cm^{-1})	Bader charge diff. of CO_2 (e)	Bader charge diff. of O (e)
O-Pt-CO_2	2	104	-29	0.05	-0.04
O-Pt_2-CO_2	0	-11	-151	-0.01	-0.10
O-Pt_3-CO_2	2	32	-34	0.05	-0.14
O-Pt_4-CO_2	2	28	-30	0.05	0.03
O-Pt_5-CO_2	0	5	64	0.05	0.02
O-Pt_{10}-CO_2	2	6	12	0.04	0.02
Pt(111)-CO_2+O [a]	0	0	0	-0.03	0.06

Differences in vibrational frequency and Bader charge are defined as (co-adsorbates - individual adsorbates). Thus positive values indicated co-adsorbates having blueshifted frequencies or possessing less charge. See Figures 4 and 6 for snapshots of the clusters.

[a] $^1/_{16}$ ML coverage each for O, O_2, CO, and CO_2. [b] $^1/_{16}$ ML coverage for CO and $^1/_8$ ML coverage for O.

Table S5: Summary of calculated (GGA-PW91) properties of NO co-adsorbed with O_2, 2O, and O and NO_2 co-adsorbed with O on Pt_x (x = 1-5 and 10) and Pt(111).

cluster	magnetic moment of system	diff. $\nu_{N\text{-}O}$ (cm^{-1})	diff. $\nu_{Pt\text{-}NO}$ (cm^{-1})	diff. $\nu_{O\text{-}O}$/ $\nu_{Pt\text{-}O}$ (cm^{-1})	Bader charge diff. of NO (e)	Bader charge diff. of O (e)
O_2-Pt-NO	1	156	2	-13	0.05	-0.08
O_2-Pt_2-NO	1	-37	56	78	0.06	0.09
O_2-Pt_3-NO	1	-97	72	-46	0.10	0.03
O_2-Pt_4-NO	1	8	-4	38	0.07	0.01
O_2-Pt_5-NO	3	11	10	72	0.04	0.04
O_2-Pt_{10}-NO	3	35	-31	21	-0.03	0.00
Pt(111)-NO+O_2 [a]	0	36	11	46	0.04	0.06
2O-Pt-NO	1	31	-112		0.25	0.25
2O-Pt_2-NO	1	37	11		0.07	0.04
2O-Pt_3-NO	1	45	25		0.12	0.01
2O-Pt_4-NO	1	-102	-12		0.12	-0.04
2O-Pt_5-NO	1	-25	1		0.02	0.01
2O-Pt_{10}-NO	1	56	-33		0.01	-0.04
Pt(111)-NO+2O [b]	0	31	14		0.07	-0.01
O-Pt-NO	1	152	-43	-9	-0.05	-0.01
O-Pt_2-NO	1	8	19	-179	-0.03	-0.11
O-Pt_3-NO	1	46	20	-37	0.11	0.08
O-Pt_4-NO	1	8	-43	-49	0.08	0.06
O-Pt_5-NO	1	6	-6	17	0.04	0.04
O-Pt_{10}-NO	3	19	-27	-20	0.02	0.02
Pt(111)-NO+O [a]	0	32	-10	-7	0.03	0.06

cluster	magnetic moment of system	diff. ν_{asONO} (cm^{-1})	diff. $\nu_{Pt\text{-}O}$ (cm^{-1})	Bader charge diff. of NO_2 (e)	Bader charge diff. of O (e)
O-Pt-NO_2	1	183	9	0.01	-0.10
O-Pt_2-NO_2	1	34	-141	-0.04	-0.04
O-Pt_3-NO_2	1	-274	0	-0.04	0.05
O-Pt_4-NO_2	1	-12	-24	0.06	0.06
O-Pt_5-NO_2	3	7	4	0.02	0.03
O-Pt_{10}-NO_2	3	44	-28	-0.10	0.03
Pt(111)-NO_2+O [a]	0	14	-10	0.03	0.06

Differences in vibrational frequency and Bader charge are defined as (co-adsorbates - individual adsorbates). Thus positive values indicated co-adsorbates having blueshifted frequencies or possessing less charge. See Figures 4 and 6 for snapshots of the clusters.

[a] $^1/_{16}$ ML coverage each for O, O_2, NO, and NO_2. [b] $^1/_{16}$ ML coverage for NO and $^1/_8$ ML coverage for O.

Table S6: Summary of calculated (DFT/PW91) properties of CO_2 and NO_2 adsorption on Pt_x (x = 1-5 and 10) and Pt(111).

cluster	magnetic moment of system	CO_2/NO_2 binding geometry	ZPE-corrected binding energy (eV)	∠ O-Y-O (º)	$d_{Y\text{-}O}$ (Å)	$\nu_{Y\text{-}O}$ (cm^{-1})	$\nu_{sY\text{-}O}$ (cm^{-1})	Bader charge of CO_2/NO_2 (e)
CO_2	0	-	-3.24 [a]	180	1.173	2357	1325	-
Pt-CO_2	0	η^2-C,O	-0.92	145	1.290; 1.193	1919	1092	-0.32
Pt_2-CO_2	2	η^2-C,O	-0.62	148	1.261; 1.193	1966	1143	-0.33
Pt_3-CO_2	2	η^2-C,O	-0.74	147	1.270; 1.199	1935	1138	-0.36
Pt_4-CO_2	2	μ-C,O	-0.81	136	1.279; 1.226	1716	1146	-0.48
Pt_5-CO_2	4	μ-C,O	-0.89	134	1.268; 1.234	1685	1191	-0.51
Pt_{10}-CO_2	6	μ-C,O	-0.11	132	1.282; 1.227	1693	1175	-0.51
Pt(111)-CO_2 [b]	0	-	0.00	180	1.173	2357	1325	0
NO_2	1	-	-1.06 [a]	134	1.213; 1.213	1658	1324	-
Pt-NO_2	1	η-N	-2.55	128	1.239; 1.239	1507	1298	-0.33
Pt_2-NO_2	1	η^2-N,O	-2.08	130	1.264; 1.217	1614	1225	-0.39
Pt_3-NO_2	1	η^2-N,O	-2.24	127	1.290; 1.220	1590	1143	-0.43
Pt_4-NO_2	1	μ-N,O	-2.51	119	1.352; 1.220	1559	903	-0.57
Pt_5-NO_2	1	μ-N,O	-2.50	118	1.362; 1.221	1560	891	-0.57
Pt_{10}-NO_2	5	η-N	-1.51	125	1.237; 1.242	1520	1304	-0.43
Pt(111)-NO_2 [b]	0	μ-N,O	-1.25	119	1.316; 1.219	1541	978	-0.45

The normal modes shown (ν) are the former asymmetric and symmetric stretch modes. The relevant properties of the free CO_2 and NO_2 molecules are included for comparison. "Y" = C or N. See Figure 5 for snapshots of the clusters.

[a] Formation energies from CO+½O_2 and NO+½O_2. [b] $^1/_{16}$ ML coverage.