ELECTRONIC SUPPLEMENTARY INFORMATION

Effects of deposited Pt particles on the reducibility of $CeO_2(111)$

Albert Bruix,[1] Annapaola Migani,[1] Georgi N. Vayssilov,[2] Konstantin M. Neyman,[*,1,3] Jörg Libuda[4,5] and Francesc Illas[*,1]

[1] *Departament de Química Física & Institut de Química Teòrica i Computacional (IQTCUB), Universitat de Barcelona, C/ Martí i Franquès 1, 08028 Barcelona, Spain*

[2] *Faculty of Chemistry, University of Sofia, 1126 Sofia, Bulgaria*

[3] *Institució Catalana de Recerca i Estudis Avançats (ICREA), 08010 Barcelona, Spain*

[4] *Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany*

[5] *Erlangen Catalysis Resource Center, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany*

[*] Corresponding authors. E-mail: konstantin.neyman@icrea.es and francesc.illas@ub.edu

Table S1: Extended Table 4. Calculated oxygen vacancy formation energies $E_f'(O_{vac})$ in four different positions (Roman numbers) of the Pt_8/CeO_2 system. For a given vacancy position (I to IV) different solutions for the electronic structure are denoted by a superindex (i.e. different number of total unpaired electrons or location and amount of Ce^{3+} centers). $|\mu|_{av}$ Ce^{3+} and $|\mu_T|$ Pt_8 correspond to the average magnitude on the Ce^{3+} cations and the total magnitude of the Pt_8 cluster, respectively, and $q(Pt_8)$ is the Bader charge of the Pt_8 cluster.

Model	Vacancy	#Ce^{3+}	$\|\mu\|_{av}$ Ce^{3+} (μ_B)	$\|\mu_T\|$ Pt_8 (μ_B)	$q(Pt_8)$	$E_f(O_{vac})$ (eV)
Opt	I^1	4	0.93	0.02	0.53	2.73
Opt	I^2	4	0.94	1.50	0.56	2.91
Opt	I^3	4	0.93	0.05	0.53	2.76
Opt	II^1	3	0.81	0.36	0.01	2.46
Opt	II^2	3	0.87	1.11	0.09	2.48
Opt	II^3	3	0.90	2.37	0.17	2.83
Opt	II^4	4	0.74	0.94	0.16	2.75
Opt	II^5	4	0.72	0.79	0.14	2.74
Opt	III^1	4	0.83	0.33	0.48	2.92
Opt	IV^1	5	0.85	0.25	0.76	2.53
Opt	IV^2	5	0.79	0.15	0.65	2.59
Opt	IV^3	4	0.90	0.10	0.63	2.62
Exp	II^1	2	0.91	0.06	-0.08	2.34
Exp	IV^1	3	0.94	0.73	0.42	2.70

Table S2: Energy (E_{spill}) of reverse spillover of an oxygen atom from the CeO_2 surface to the supported Pt_8 cluster at the most stable positions of the vacancy O_{vac} and adsorbed atom O_{ads}. $|\mu|_{av}$ Ce^{3+} and $|\mu_T|$ Pt_8 correspond to the average magnitude on the Ce^{3+} cations and the total magnitude of the Pt_8 cluster, respectively. $q(Pt_8)$ is the Bader charge of the Pt_8 cluster.

Model	O_{vac}	O_{ads}	#Ce^{3+}	$\|\mu\|_{av}$ Ce^{3+} (μ_B)	$\|\mu_T\|$ Pt_8 (μ_B)	$q(Pt_8)$	E_{spill} (eV)
Opt	II	Pt_2	3	0.85	1.03	0.79	1.00
Opt	II	Pt_3	3	0.82	0.32	0.88	1.24
Opt	IV	Pt_2	4	0.89	1.24	1.34	1.25
Exp	II	Pt_2	3	0.82	0.93	0.82	1.00

Table S3: Energy (E_{ads}) of oxygen adsorption computed with respect to $1/2O_2$ at various O_{ads} positions of the Pt_8 cluster supported on $CeO_2(111)$. $|\mu|_{av}$ Ce^{3+} and $|\mu_T|$ Pt_8 correspond to the average magnitude on the Ce^{3+} cations and the total magnitude of the Pt_8 cluster, respectively and $q(Pt_8)$ is the Bader charge of the Pt_8 cluster.

O_{ads}	$\#Ce^{3+}$	$\|\mu\|_{av}$ Ce^{3+} (μ_B)	$\|\mu_T\|$ Pt_8 (μ_B)	$q(Pt_8)$	E_{ads} (eV)
Pt_3	2	0.85	1.03	1.55	-1.16
Pt_2	2	0.93	1.38	1.43	-1.30

Figure S1: Top (left panels) and side (right panels) views of the most stable computed $Pt_8/CeO_{2-x}(111)$ structures with an oxygen atom removed from different positions (I-IV) of the slab to the gas-phase. Red spheres – O, purple – Ce, blue – Pt, yellow and light blue – spin density.

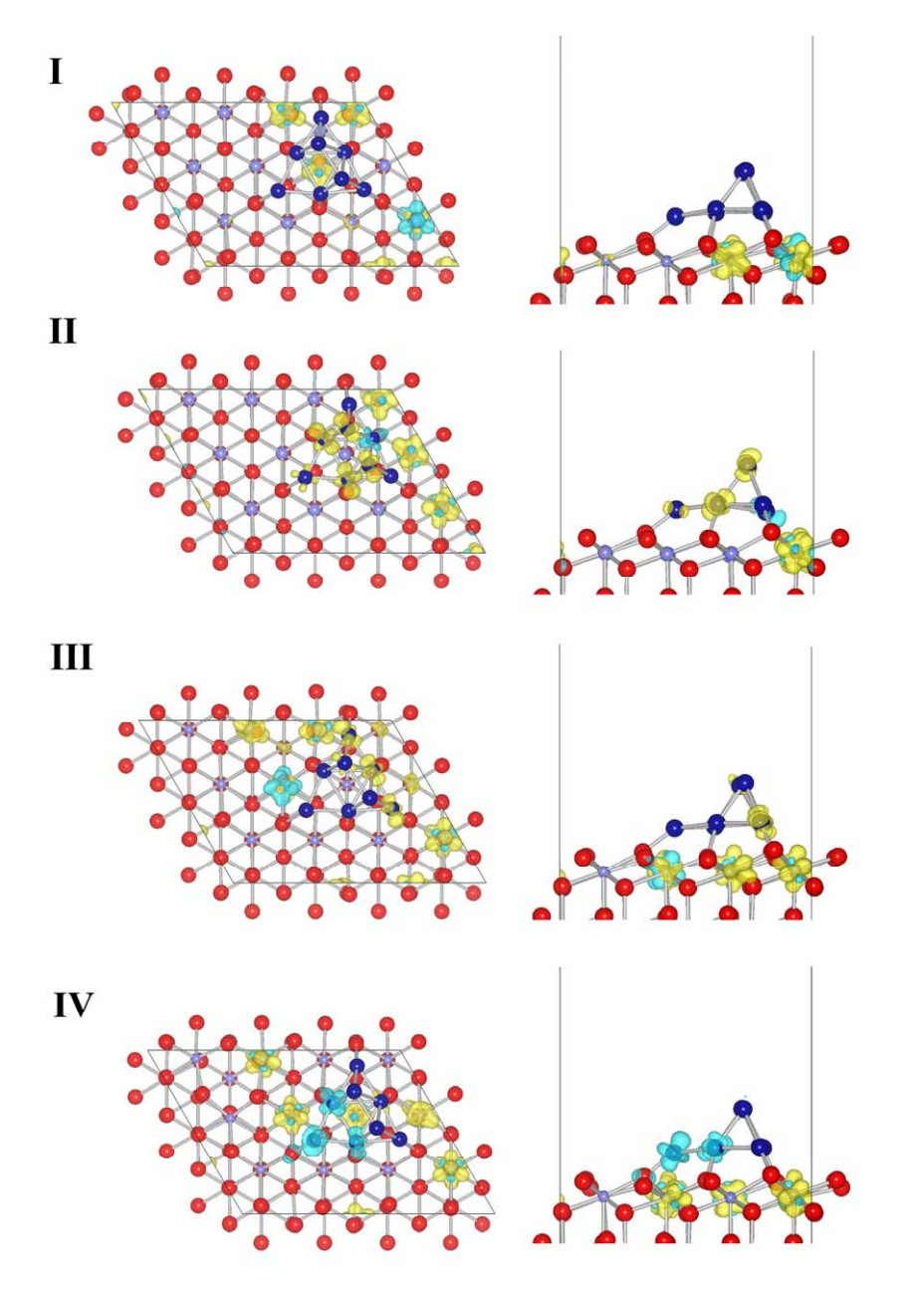

Figure S2: Top (left panels) and side (right panels) views of the most stable computed O-Pt_8/CeO_{2-x}(111) structures with an oxygen atom spilled-over from two different positions (II and IV) of the slab and adsorbed on different stable sites (Pt_2 and Pt_3) of the Pt_8 particle. Red spheres – O, purple – Ce, blue – Pt, yellow and light blue – spin density.