Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information to "Atomically dispersed platinum on low index and stepped ceria surfaces: phase diagrams and stability analysis"

Xing Wang,[†,‡] Jeroen A. van Bokhoven,[†,‡] and Dennis Palagin[*,‡]

†*Institute for Chemical and Bioengineering, ETH Zurich, Vladimir Prelog Weg 1, 8093 Zurich, Switzerland*

‡*Laboratory for Catalysis and Sustainable Chemistry, Paul Scherrer Institute, 5232 Villigen-PSI, Switzerland*

E-mail: dennis.palagin@psi.ch

SI *U* term

Hubbard-type U term was tested for different properties of ceria (cell parameters, bulk modulus, band gaps, and reaction energies) as shown in Table S1. Specifically, the following reaction energies (eq. 1 and 2) were used as references, due to their importance in the redox chemistry of ceria. A U value of 4.5 eV was used in order to get a balanced description.

$$2CeO_2 \longrightarrow Ce_2O_3 + \frac{1}{2}O_2 \tag{1}$$

$$2CeO_2 + H_2 \longrightarrow Ce_2O_3 + H_2O \tag{2}$$

Table S1: Lattice parameters (Å), bulk modulus B (GPa), bandgap (eV) (O 2p-Ce 4f for CeO_2 and Ce 4f-Ce 5d for Ce_2O_3) and energies (kJ/mol) of formation for CeO_2 and Ce_2O_3 and energies of reduction (eqs 1 and 2) obtained with different methods. U values are specified where applicable.

		CeO_2			Ce_2O_3				eq 1	eq 2	ref
Methods	U (eV)	a	B	bandgap	a	c	B	bandgap	$\Delta E_r 1$	$\Delta E_r 2$	
PBE + U	2	5.413	194	2.84	3.838	6.121	132	0.78	468	221	
PBE + U	3	5.412	196	3.01	3.854	6.130	135	1.38	437	189	
PBE + U	4	5.411	198	3.19	3.869	6.114	136	1.97	396	148	
PBE + U	5	5.410	200	3.39	3.871	6.098	137	2.61	355	108	
PBE + U	6	5.410	202	3.59	3.873	6.117	136	3.13	324	77	
PBE + U	7	5.409	204	3.80	3.874	6.114	136	3.48	292	44	
PBE + U	8	5.409	205	4.01	3.876	6.111	136	3.72	259	11	
HSE	-	5.40	-	3.50	3.87	6.07	-	2.50	306	-	[1]
Exp.	-	5.410	204-237	3.16	3.890	6.060	-	2.40	388	149	[2,3]

SII Bader charge

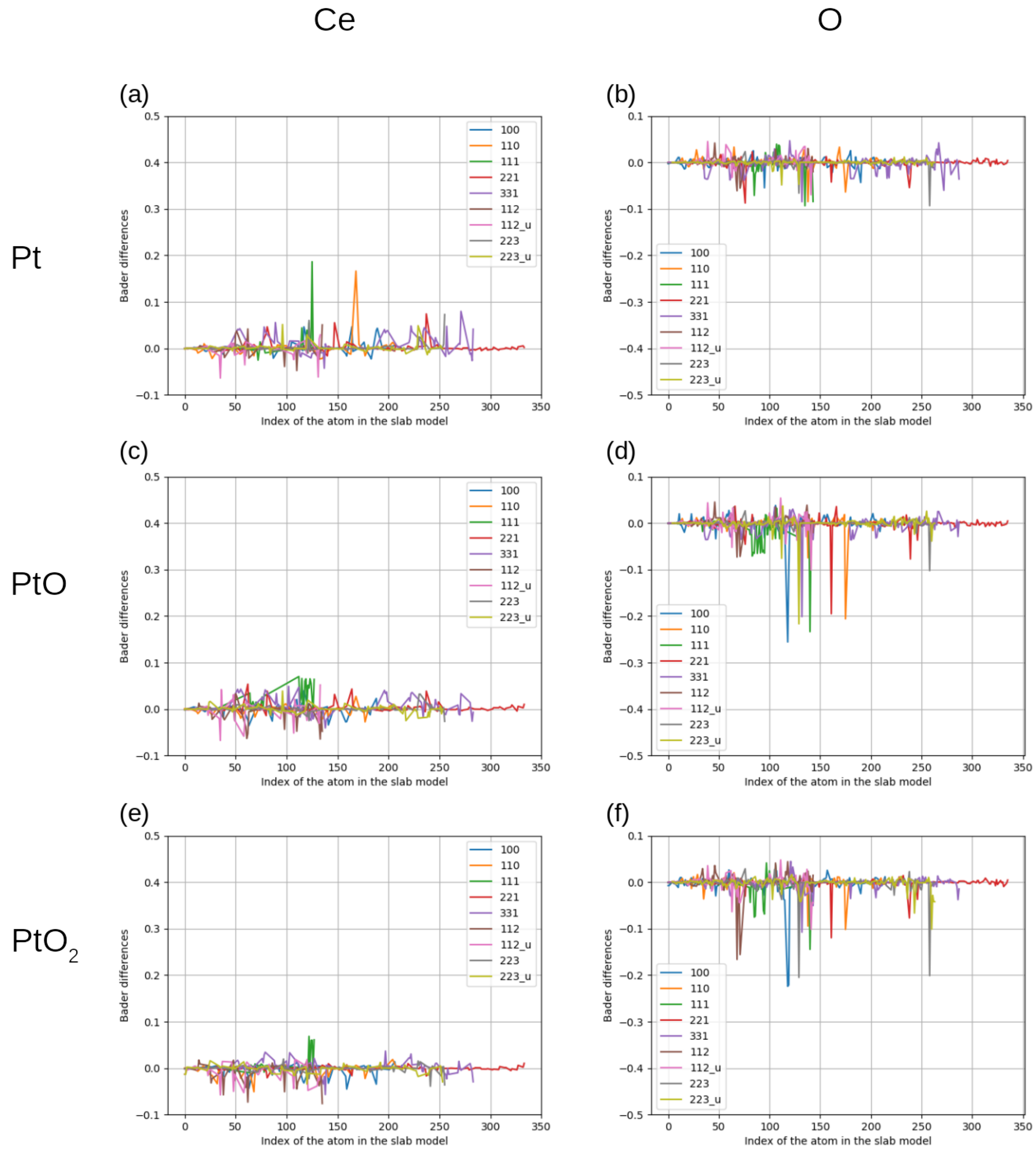

Figure S1: Bader charge differences of cerium and oxygen atoms in the surface models before and after PtO_x adsorption. In all cases, singlet states are found to be the most stable configurations.

Table S2: Bader charges differences of adjacent Ce atoms (Pt-Ce bond smaller than 3.5 Å) in the surface models before and after PtO_x adsorption. Bader charge difference between Ce^{4+} and Ce^{3+} is around 0.3 |e|. No Ce^{3+} is formed on the ceria surfaces.

Surf	$(\mathrm{Pt})_{\mathrm{ads}}$	$(\mathrm{PtO})_{\mathrm{ads}}$	$(\mathrm{PtO}_2)_{\mathrm{ads}}$
100	$0.05, 0.05, 0.04, 0.04$	$0.02, 0.04, -0.03, 0.02$	$-0.03, -0.03, -0.03, -0.03$
110	$-0.01, -0.02, -0.01, 0.17, -0.02$	$0.00, -0.00, 0.03$	$-0.03, -0.05, 0.01$
111	$0.04, 0.04, 0.19$	$0.02, 0.07$	
221	$0.02, 0.05, 0.06, 0.07$	$0.05, 0.04, 0.04$	$-0.02, 0.00, -0.02$
331	$0.02, 0.05, 0.08, 0.04$	$0.05, 0.03, -0.01$	$0.01, -0.01, -0.06$
112	$0.03, 0.04, 0.04, 0.05$	$0.03, 0.03, -0.05, -0.05$	$-0.07, -0.08$
112^b	$0.01, 0.02, 0.02, 0.03$	$0.03, -0.01, -0.03, 0.05$	$-0.05, -0.05, -0.03, -0.01$
223	$0.06, 0.02, 0.02, 0.07$	$-0.03, 0.03, 0.03, -0.03$	$-0.02, -0.04$
223^b	$0.05, 0.03, 0.02, 0.05$	$0.04, 0.01, 0.02, -0.02$	$-0.03, -0.01, -0.02, -0.03$

SIII Stability of Pt^+ species

On stoichiometric ceria surfaces, a Ce^{4+} ion can accept an electron from the adsorbed platinum atom, and become Ce^{3+}:

$$[\mathrm{Ce}^{4+}, 2\,\mathrm{O}^{2-}]/\mathrm{Pt}^0 \longrightarrow [\mathrm{Ce}^{3+}, 2\,\mathrm{O}^{2-}]/\mathrm{Pt}^+ \tag{3}$$

To study different possible electron configurations of the system, both singlet and triplet states are considered, which correspond to the adsorption processes with and without electron transfer from the platinum atom to the ceria substrate, respectively. DFT predicted correct energy order for atomic platinum in gas phase. Open-shell triplet ($5\mathrm{d}^9 6\mathrm{s}^1$) is more stable (−0.49 eV) than the closed-shell singlet ($5\mathrm{d}^{10}$). After platinum atoms adsorbed on ceria surfaces, the singlet state becomes slightly more stable than the triplet state (see Figure S3). This is consistent with previously reported data.[4] Magnetic moments of platinum in $(\mathrm{Pt})_{\mathrm{ads}}/\mathrm{CeO}_2(100)$ are 0 μ_B and 0.52 μ_B for the singlet state and triplet state, respectively. Adding +U to both cerium and platinum cores leads to numerical convergence problems during the calculations. As the singlet state has been shown to be more stable for adsorbed species,[4] and taking into account that platinum atoms in singlet state does not feature partially unoccupied d-orbitals, thus the +U term is not added to platinum atoms.

Figure S2 shows the triplet state for the platinum atom on the CeO_2 (100) surface, which resulted in different positions of the Ce^{3+} atoms and different nature of their f-type orbitals. Using $U = 3$ eV leads to excessively delocalized f electrons for the triplet state, with the electron transferred from platinum being shared by various Ce cations. Hence, such low values are not suitable to describe the localized character of the strongly correlated electrons. On the other hand, using larger U values (9 eV) results in the same Ce^{3+} positions as $U = 4.5$ eV. However, as discussed in section SI, larger U value will give wrong reaction energy of bulk ceria phases.

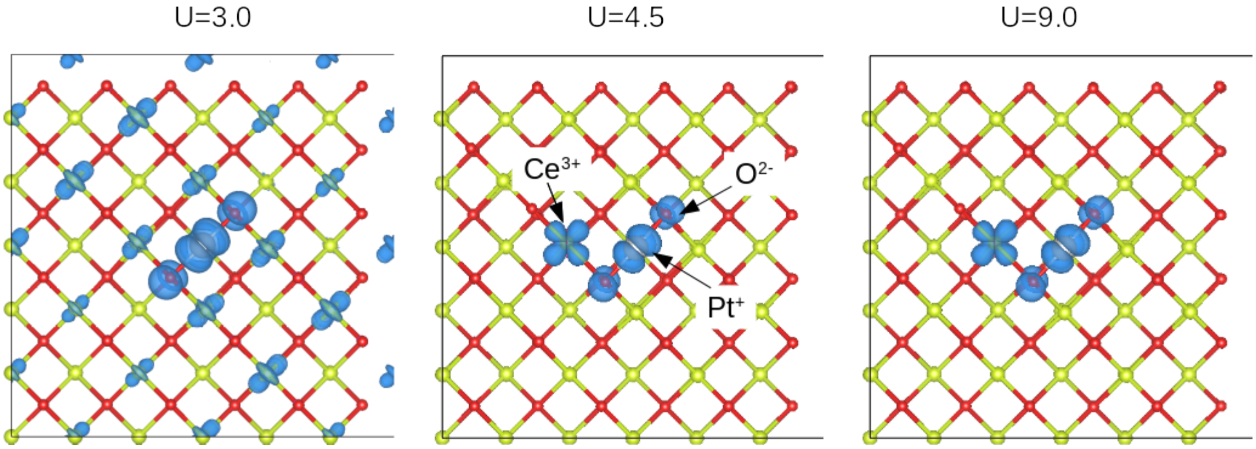

Figure S2: Spin configurations in CeO_2 (100) surface with a platinum atom on the surface for different U values at triplet state. Positions of the Ce^{3+} atoms are indicated by their occupied 4f orbitals.

Figure S3 presents the stability of the Pt^+ (triplet state) in the most stable geometry on ceria surfaces (as shown in the main text) at different U values (from 3 to 9 eV). The reference state is the Pt^0 (singlet state). Increasing the value of U stabilizes the presence of f electrons, and leads to a progressive stabilization of the Pt^+ state. Such an increase eventually leads to an inversion of the relative stability at centain U value, for which the Pt^+ is more stable than the Pt^0. At the U value (4.5 eV) we used, all Pt^+ species are not stable compared to Pt^0. We also note that Ce^{3+} is more easyly to formed at the stepped surface.

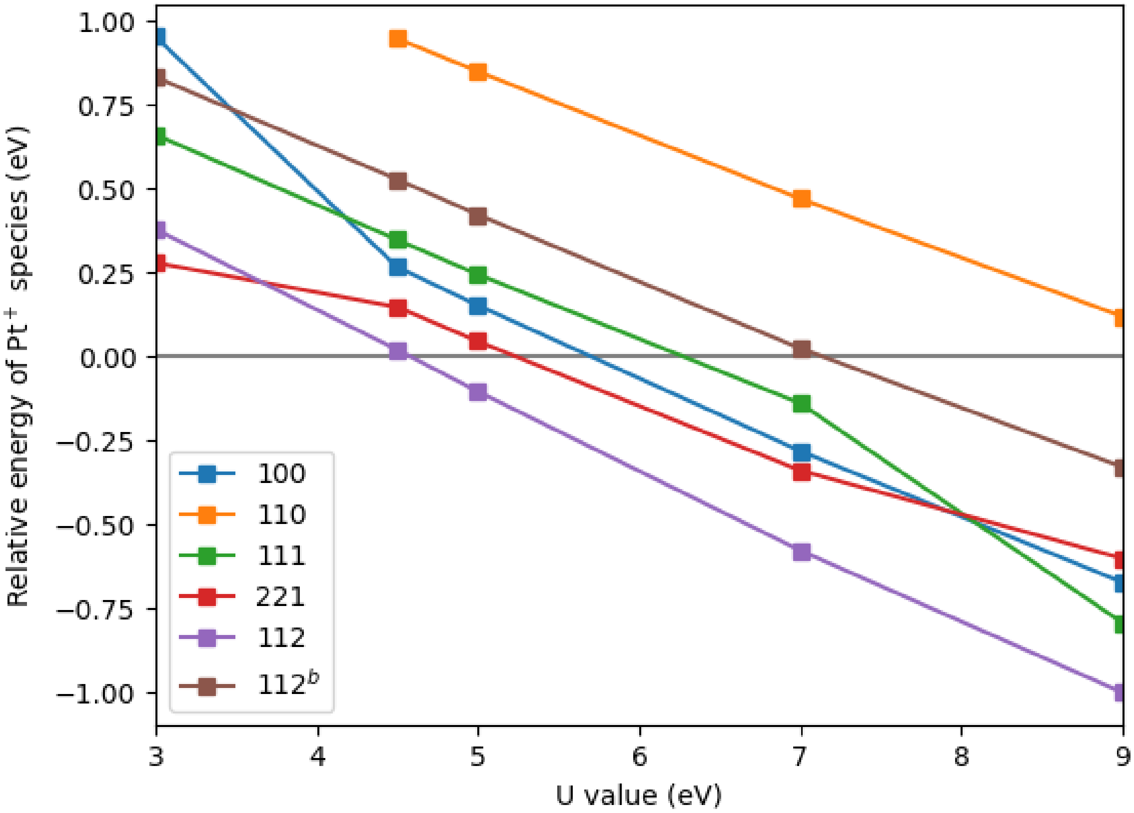

Figure S3: Relative stability of Pt^{+} (triplet state) species on the ceria surfaces with different U values. The reference state is the Pt^{0} (singlet state).

SIV Structure

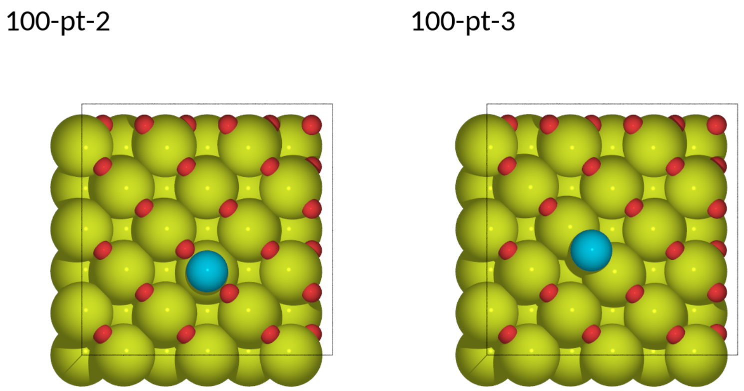

Figure S4: Optimized structures of Pt on CeO_2 (100) surface. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

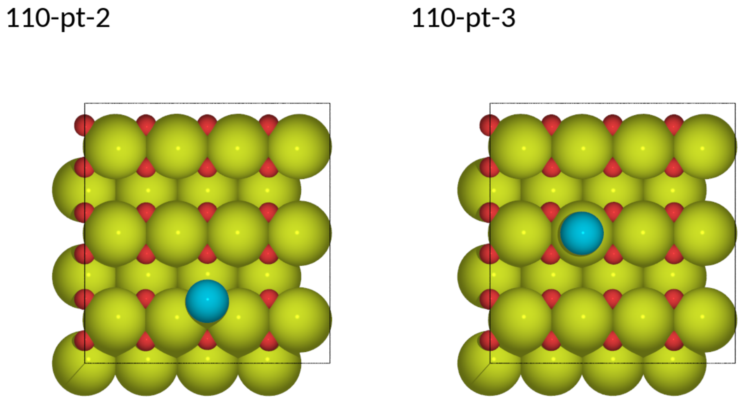

Figure S5: Optimized structures of Pt on CeO_2 (110) surface. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

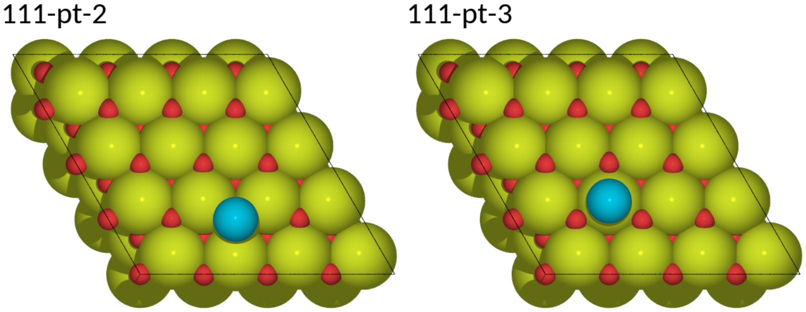

Figure S6: Optimized structures of Pt on CeO_2 (111) surface. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

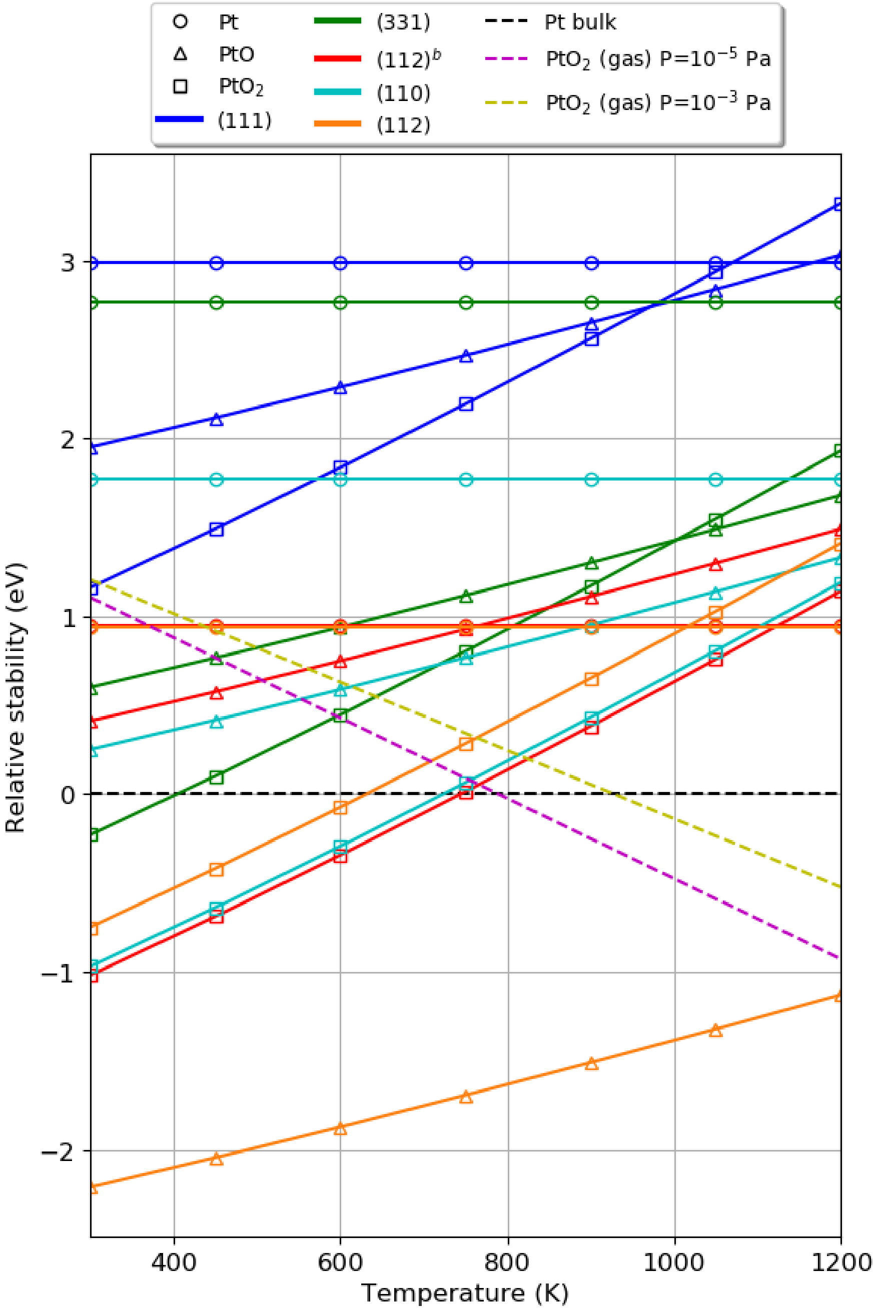

Figure S7: Relative stability of PtO$_x$ (x=0, 1, 2) phases on ceria surfaces compared to bulk platinum and PtO$_2$ gas phase. Symbols (circle: (Pt)$_{ads}$; triangle: (PtO)$_{ads}$; square: (PtO$_2$)$_{ads}$) on each colored line correspond to the PtO$_x$ species adsorbed on a corresponding surface.

SV Effects of coverage

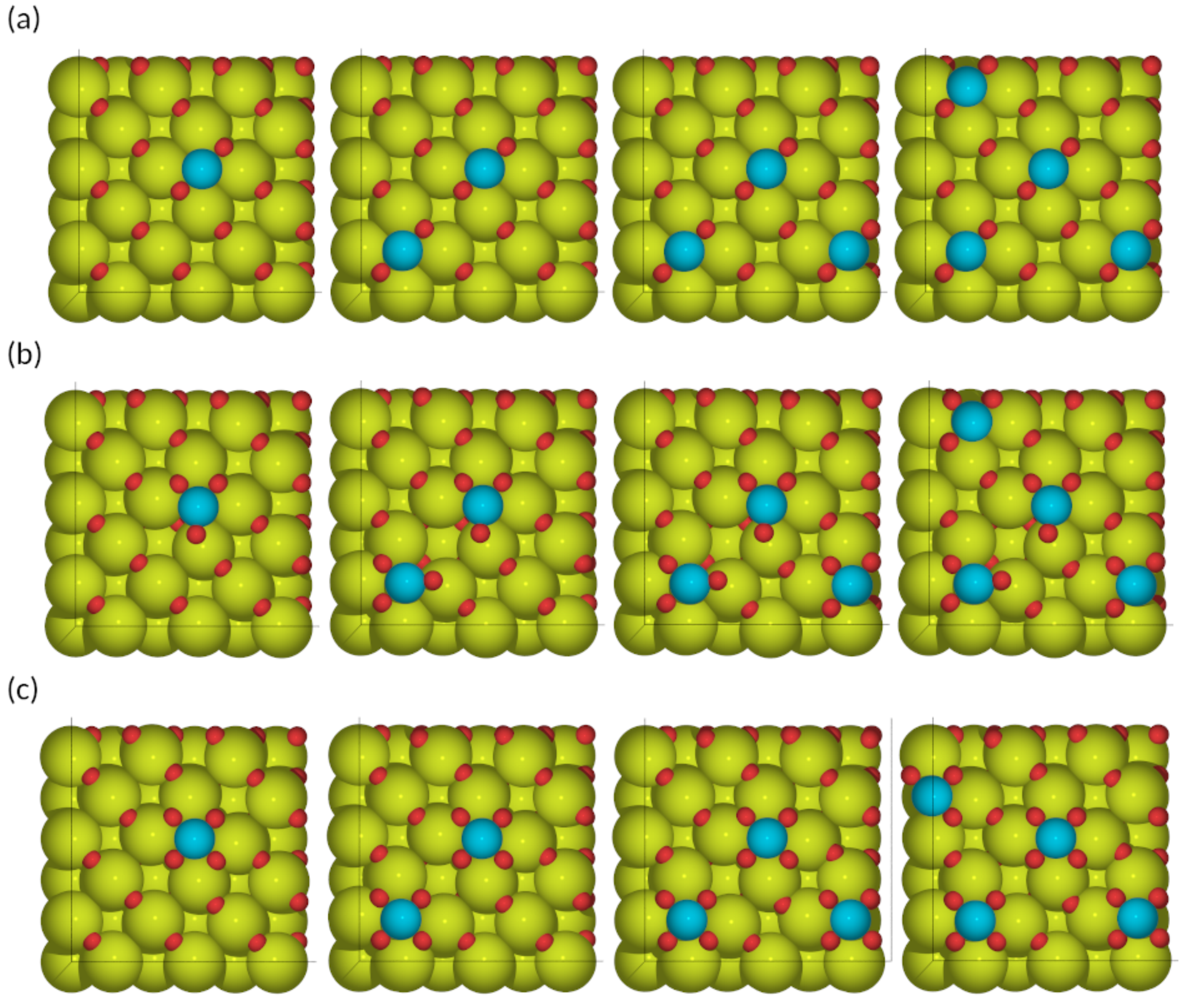

Figure S8: Optimized structures of PtO_x (x=0, 1, 2) on CeO_2 (100) surface at different coverage. (a) $(Pt)_{ads}$; (b) $(PtO)_{ads}$; (c) $(PtO_2)_{ads}$. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

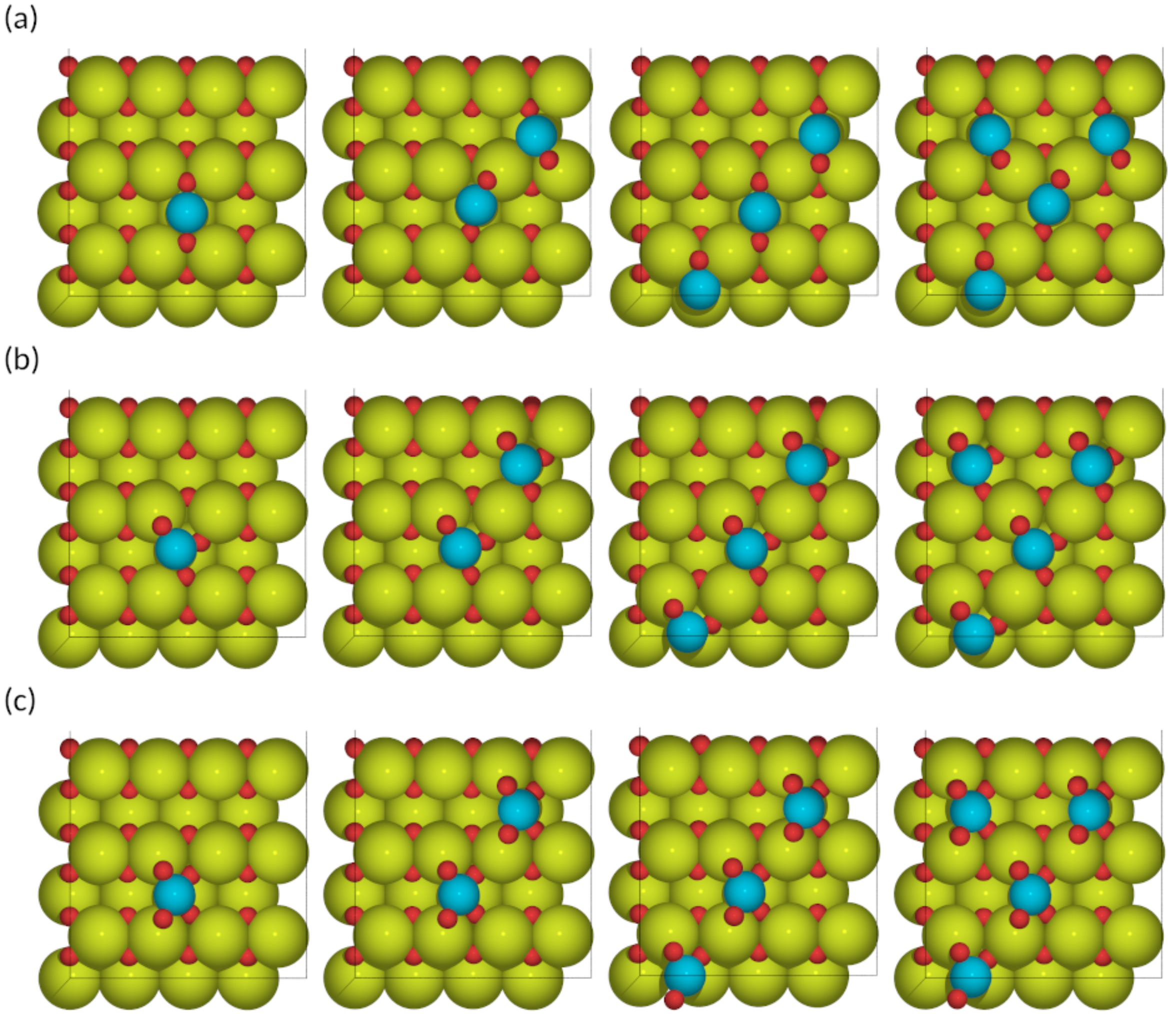

Figure S9: Optimized structures of PtO_x (x=0, 1, 2) on CeO_2 (110) surface at different coverage. (a) $(Pt)_{ads}$; (b) $(PtO)_{ads}$; (c) $(PtO_2)_{ads}$. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

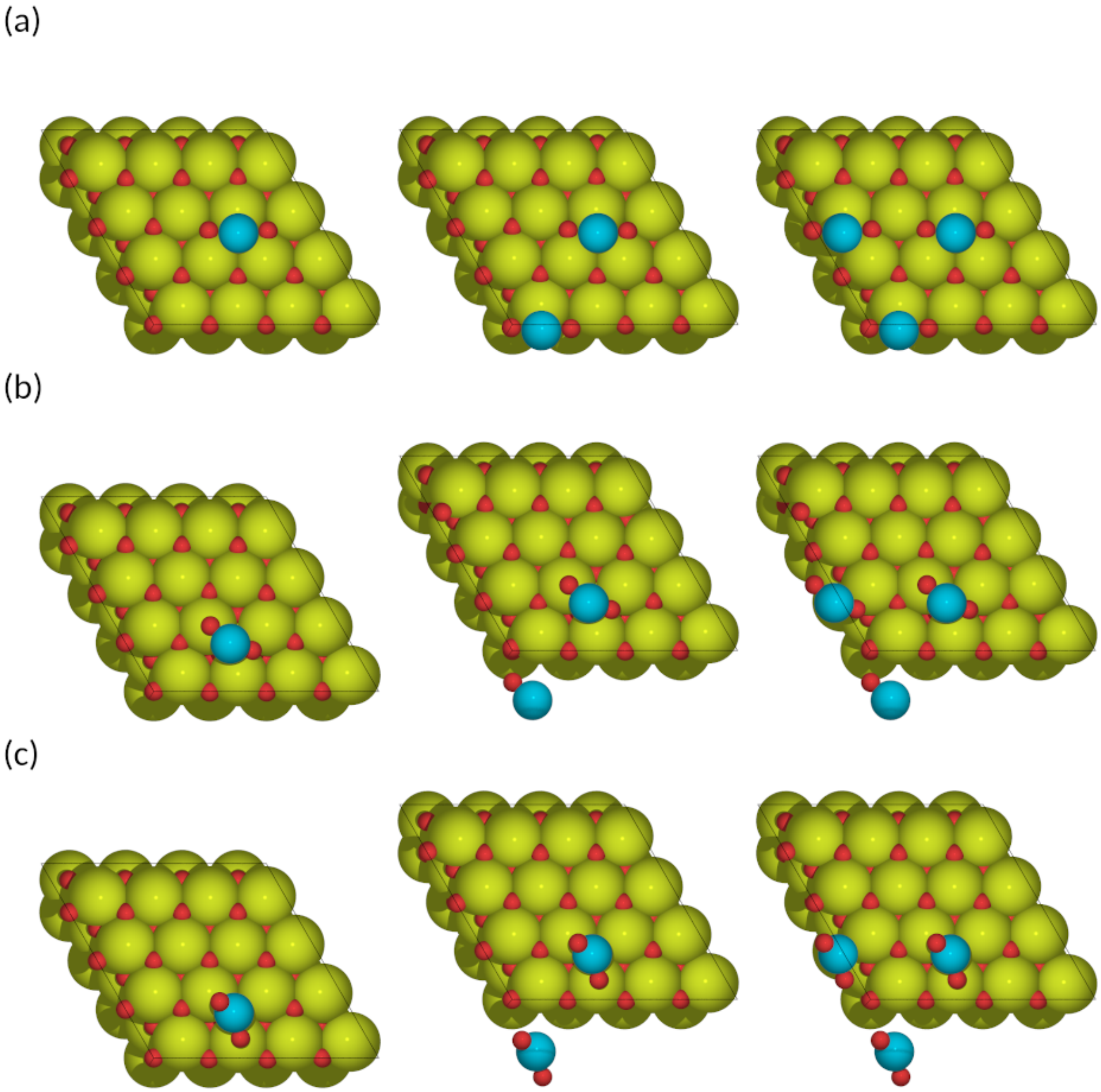

Figure S10: Optimized structures of PtO_x (x=0, 1, 2) on CeO_2 (111) surface at different coverage. (a) $(Pt)_{ads}$; (b) $(PtO)_{ads}$; (c) $(PtO_2)_{ads}$. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

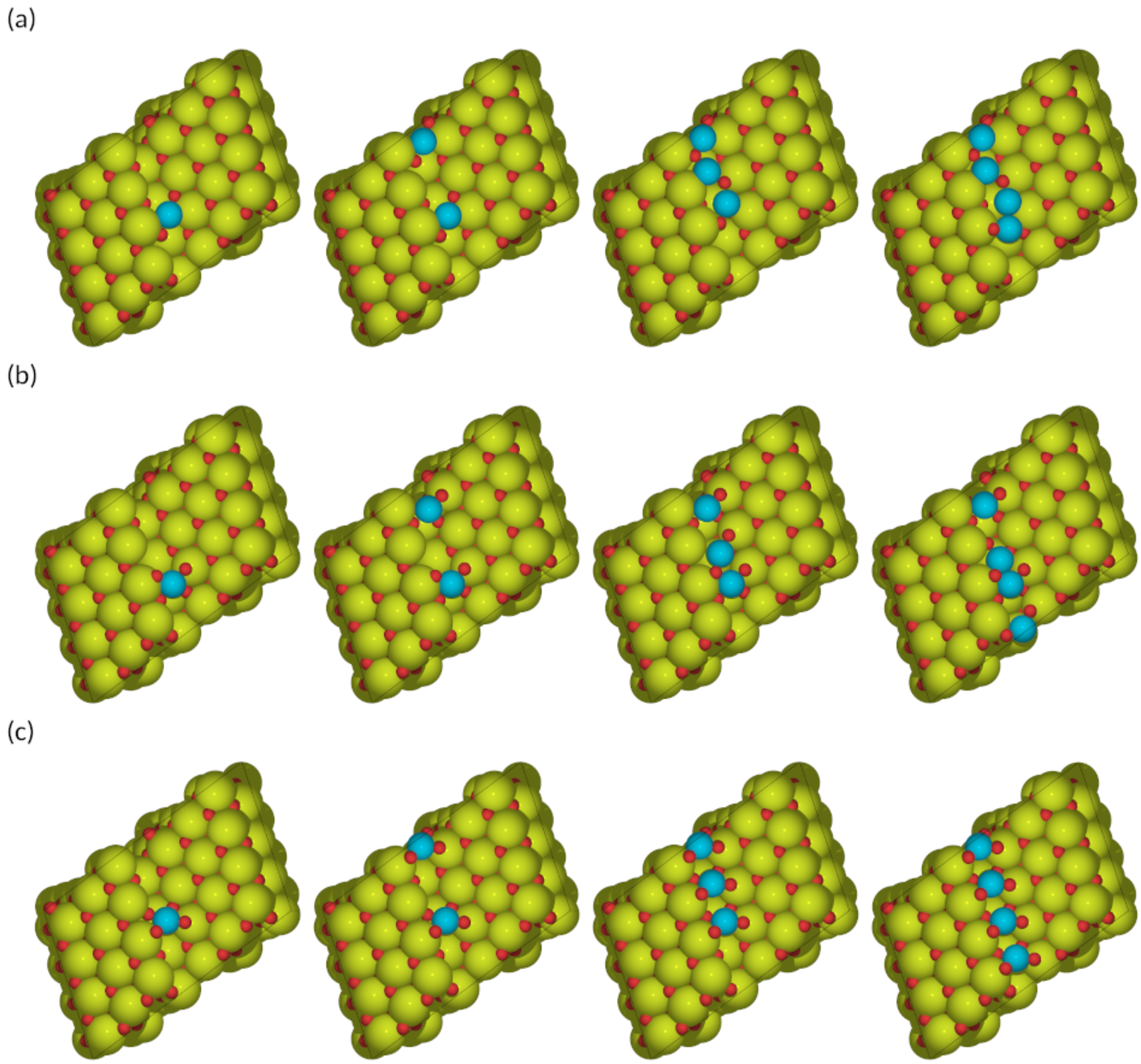

Figure S11: Optimized structures of PtO_x (x=0, 1, 2) on CeO_2 (221) surface at different coverage. (a) $(Pt)_{ads}$; (b) $(PtO)_{ads}$; (c) $(PtO_2)_{ads}$. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

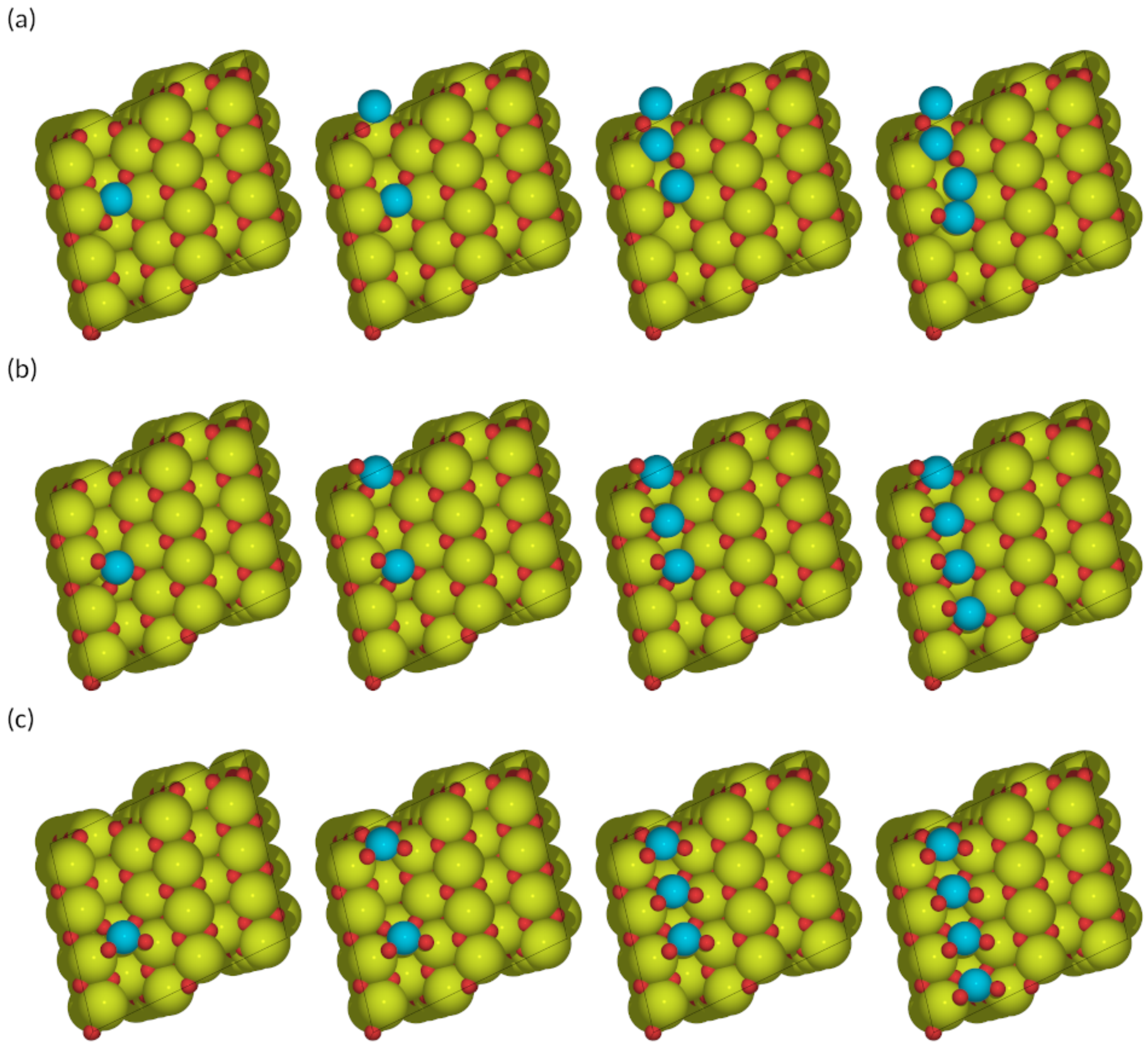

Figure S12: Optimized structures of PtO_x (x=0, 1, 2) on CeO_2 (331) surface at different coverage. (a) $(Pt)_{ads}$; (b) $(PtO)_{ads}$; (c) $(PtO_2)_{ads}$. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

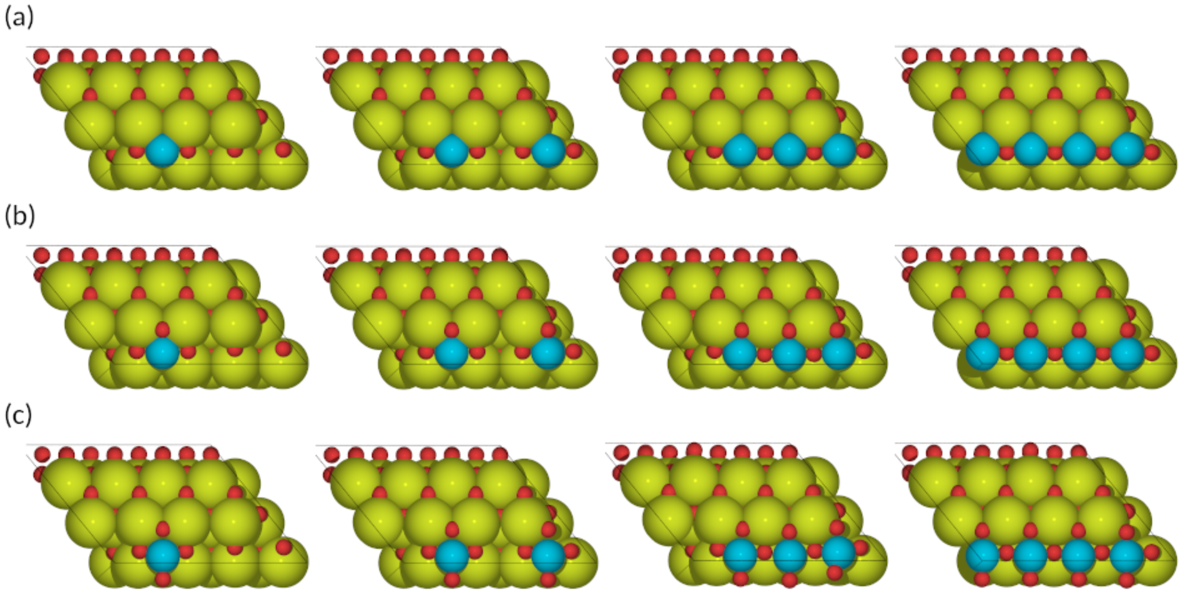

Figure S13: Optimized structures of PtO_x (x=0, 1, 2) on CeO_2 (112) surface at different coverage. (a) $(Pt)_{ads}$; (b) $(PtO)_{ads}$; (c) $(PtO_2)_{ads}$. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

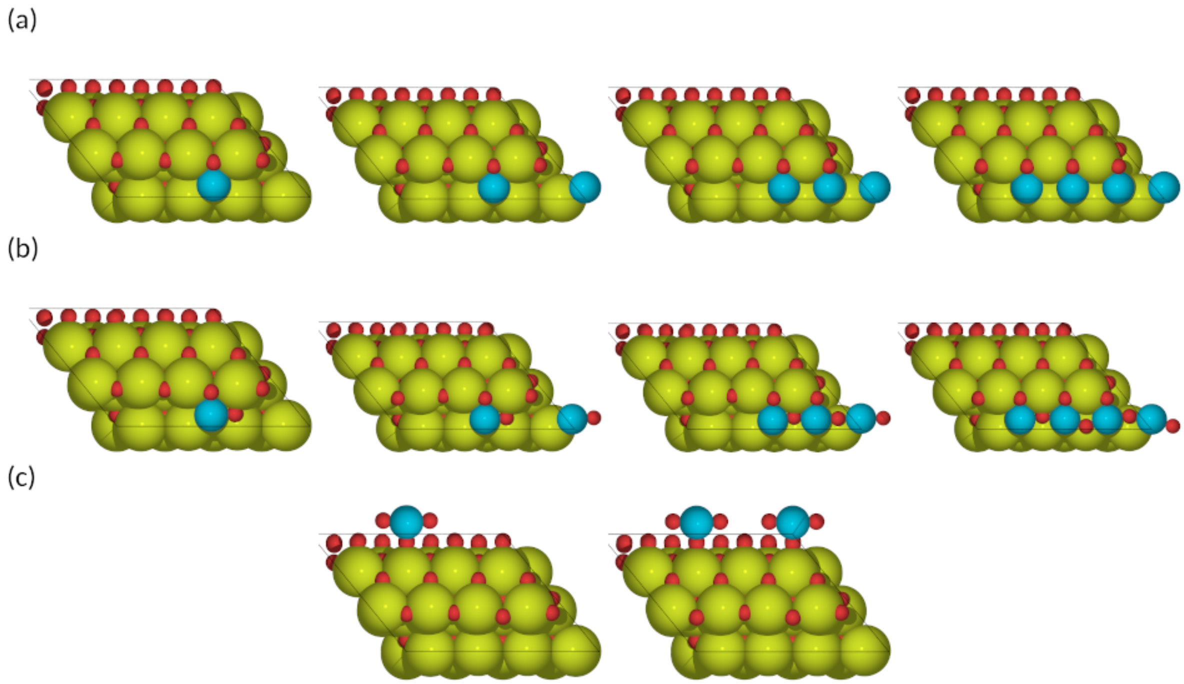

Figure S14: Optimized structures of PtO_x (x=0, 1, 2) on CeO_2 $(112)^b$ surface at different coverage. (a) $(Pt)_{ads}$; (b) $(PtO)_{ads}$; (c) $(PtO_2)_{ads}$. At high coverages, one oxygen atom from the $(PtO)_{ads}$ species connects with the neighboring platinum atom, forming a square-planar $[PtO_4]$ chain on the step site. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

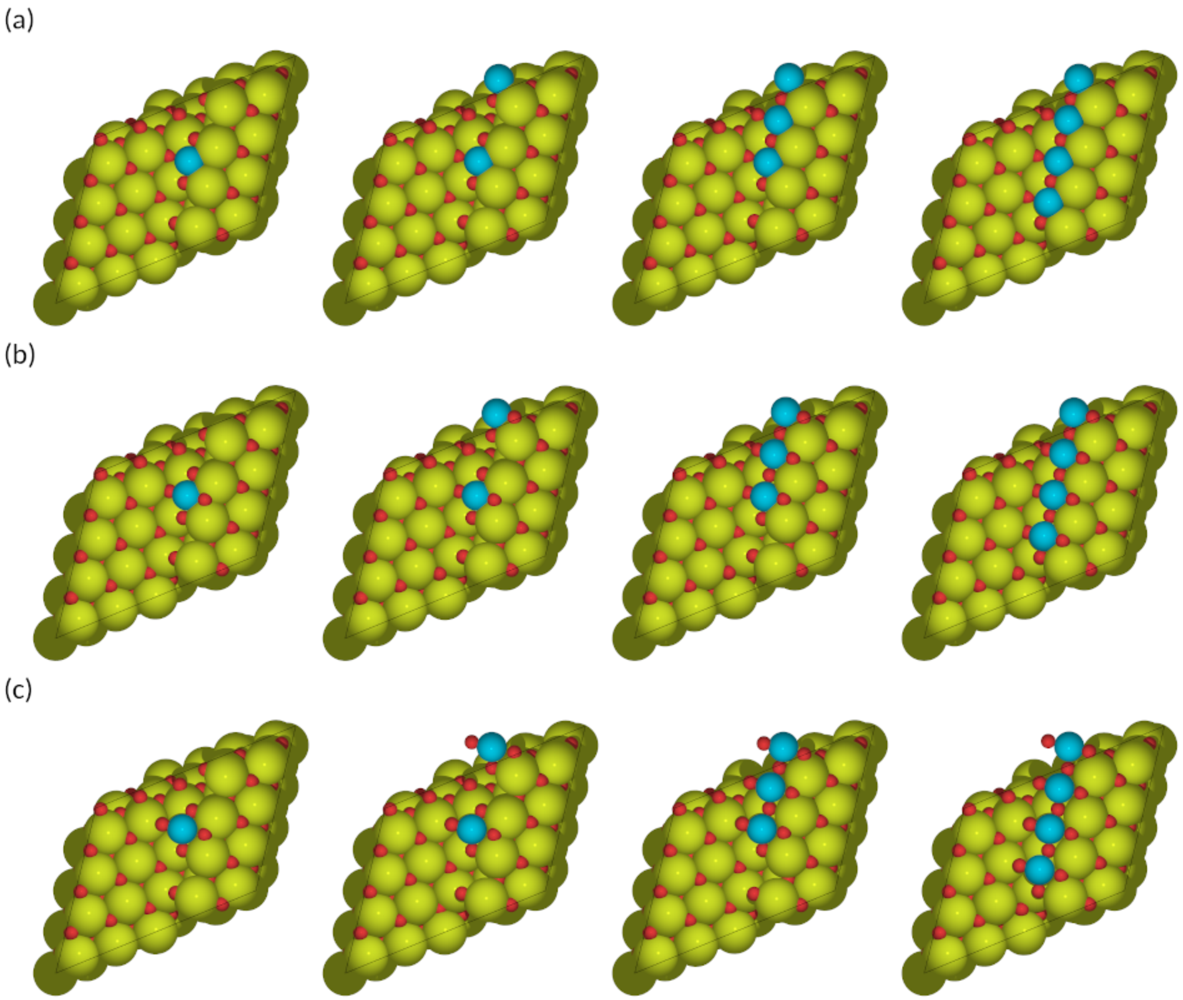

Figure S15: Optimized structures of PtO_x (x=0, 1, 2) on CeO_2 (223) surface at different coverage. (a) $(Pt)_{ads}$; (b) $(PtO)_{ads}$; (c) $(PtO_2)_{ads}$. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

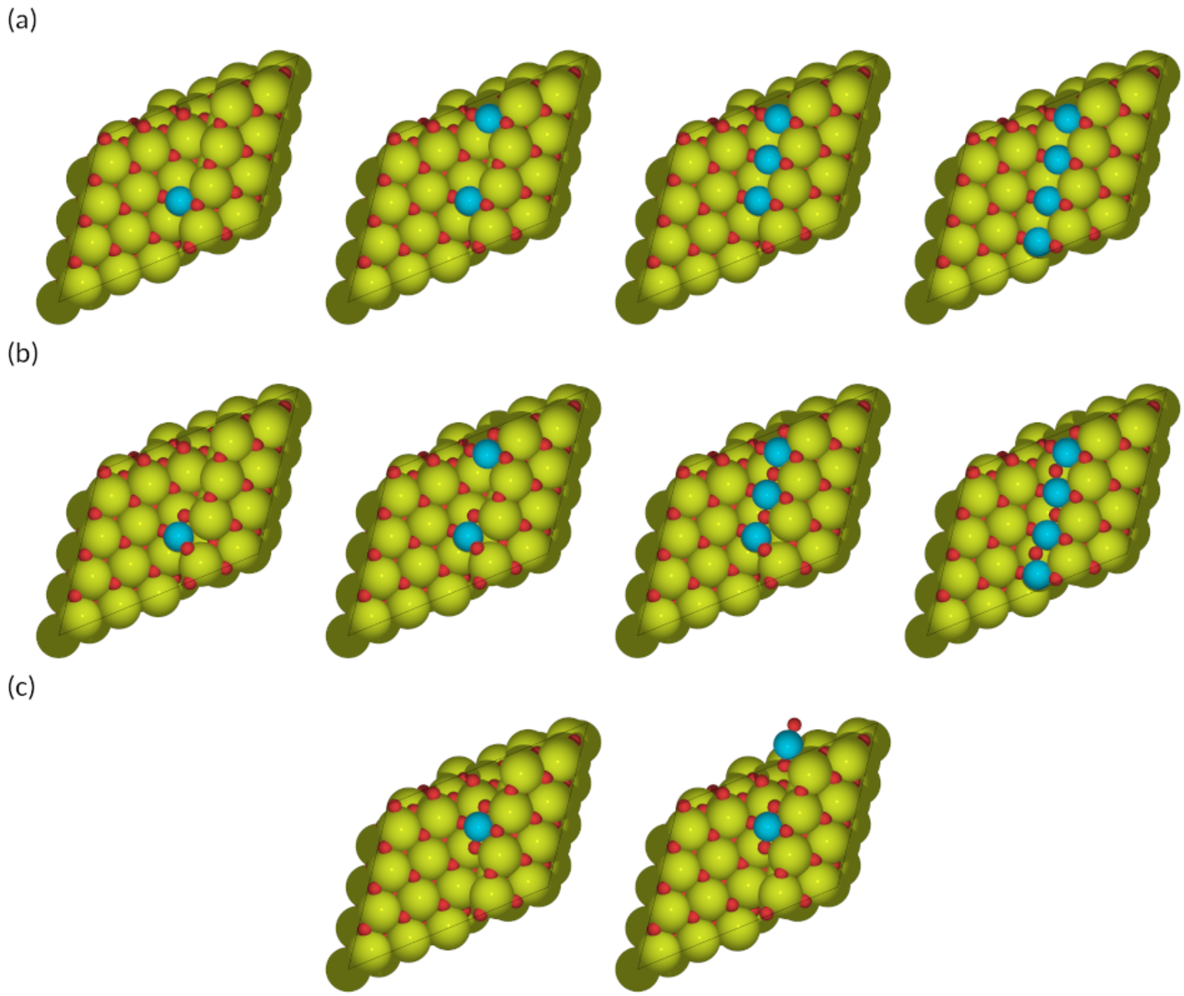

Figure S16: Optimized structures of PtO_x (x=0, 1, 2) on CeO_2 $(223)^b$ surface at different coverage. (a) $(Pt)_{ads}$; (b) $(PtO)_{ads}$; (c) $(PtO_2)_{ads}$. At high coverages, one oxygen atom from the $(PtO)_{ads}$ species connects with the neighboring platinum atom, forming a square-planar $[PtO_4]$ chain on the step site. Green spheres indicate Ce atoms, blue ones are platinum atoms, while red ones are oxygen atoms.

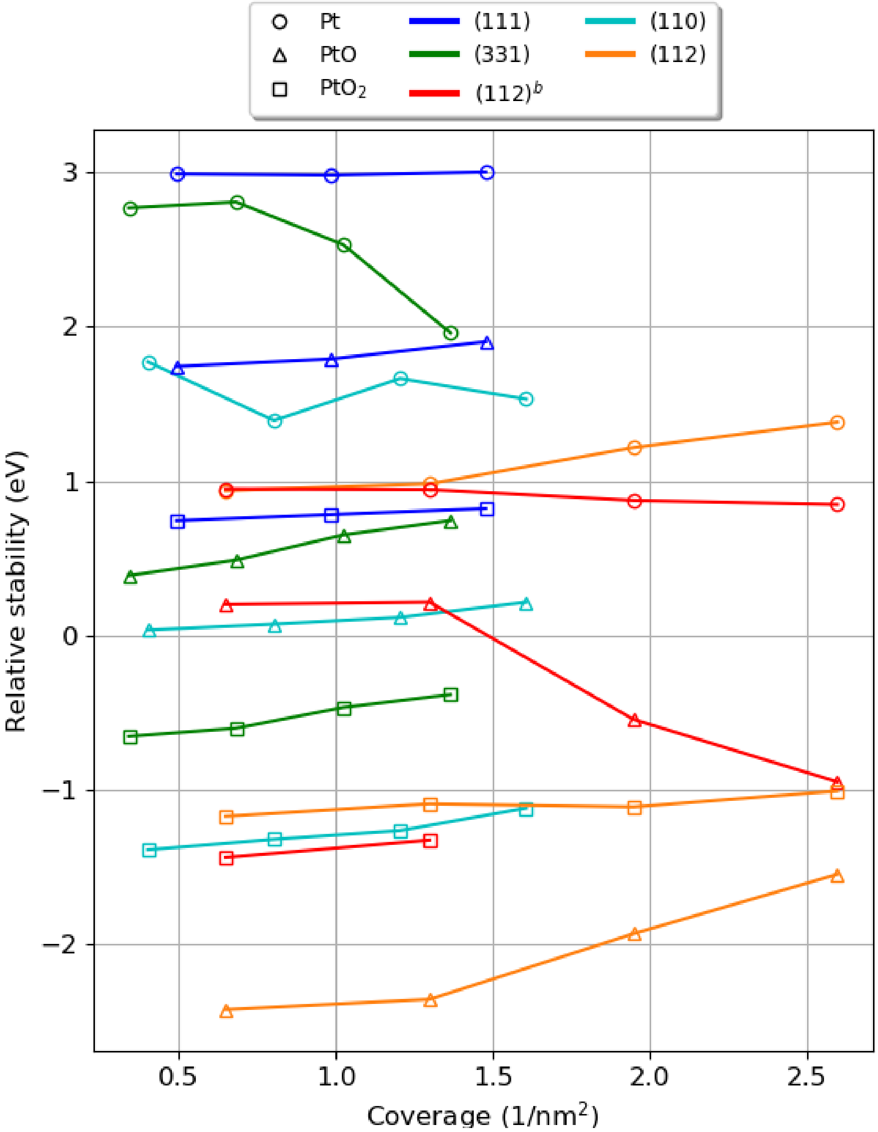

Figure S17: Relative stability of $(PtO_x)_{ads}$ (x=0, 1, 2) phases on ceria surfaces compared to bulk platinum change with coverage. Symbols (circle: $(Pt)_{ads}$; triangle: $(PtO)_{ads}$; square: $(PtO_2)_{ads}$) on each colored line correspond to the PtO_x species adsorbed on a corresponding surface.

References

[S1] Da Silva, J. L. F.; Ganduglia-Pirovano, M. V.; Sauer, J.; Bayer, V.; Kresse, G. Hybrid functionals applied to rare-earth oxides: The example of ceria. *Phys. Rev. B* **2007**, *75*, 045121.

[S2] Bärnighausen, H.; Schiller, G. The crystal structure of A-Ce2O3. *J. Less. Common. Met.* **1985**, *110*, 385–390.

[S3] Gerward, L.; Staun Olsen, J.; Petit, L.; Vaitheeswaran, G.; Kanchana, V.; Svane, A. Bulk modulus of CeO2 and PrO2—An experimental and theoretical study. *J. Alloy Compd.* **2005**, *400*, 56–61.

[S4] Bruix, A.; Neyman, K. M.; Illas, F. Adsorption, Oxidation State, and Diffusion of Pt Atoms on the CeO2(111) Surface. *J. Phys. Chem. C* **2010**, *114*, 14202–14207.