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Supplementary Information to "Ostwald ripening versus single atom trapping: towards understanding platinum particles sintering"

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SI Test for the U value

In the present study, four U values ($U = 3, 4, 5, 7$ eV) are considered, as is shown in Table Table S1. The difference of binding energy for all the U values are smaller than 0.06 eV, which indicates that the U value has only a small effect on the binding energy.

Table S1: Binding energy of PtO_2 adsorbed on CeO_2 surfaces with different U value. The enrgies are given with respect to the value at $U = 7$. The adsorption site corresponds to the most stable configuration.

U value (eV)	Binding energy (eV)	
	CeO_2 (111)	CeO_2 (111) step
3	0.04	0.06
4	0.02	0.03
5	0.03	0.04
7	0.0	0.0

SII PtO_2(g) on Pt(111) surfaces

The p(4 × 4) cell of Pt(111) surface is modeled as periodically repeated slabs with four layers. The bottom two atomic layers are kept frozen and set to the bulk parameters, while the remaining layers are fully relaxed during the calculations. The cell has dimensions of a=b=11.22 Å and c=25 Å, which includes a vacuum region of thickness higher than 15 Å and guarantees no interactions between the slabs. Therefore, in the present study we only use the computationally less expensive p(4 × 4) model of the Pt(111) surface.

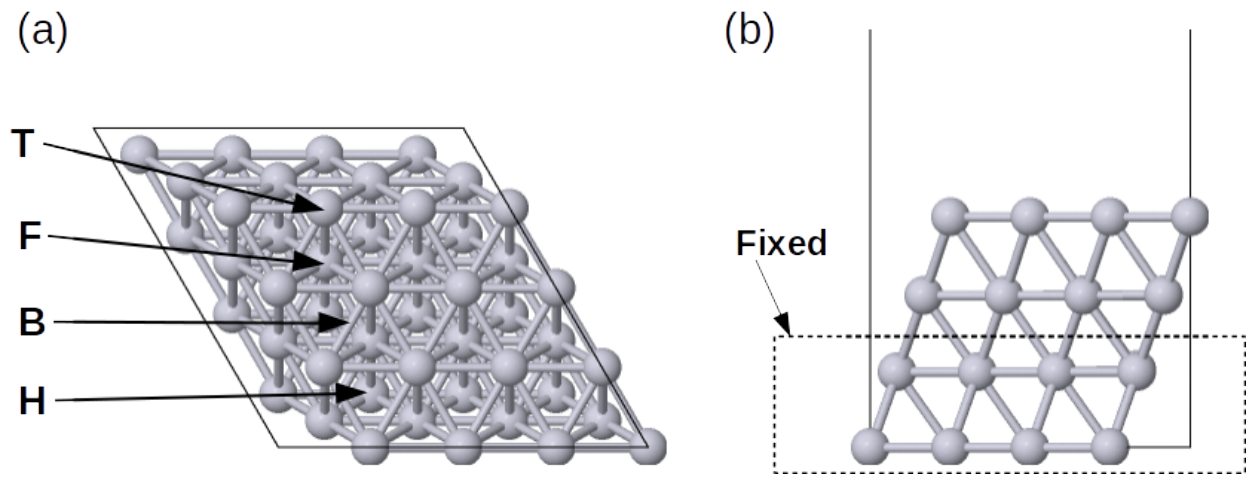

Figure S1: (a) Top and (b) cross-sectional view of the Pt(111) surface. The adsorption sites are labeled as top (T), bridge (B), fcc (F), and hcp (H) sites.

The coordination of PtO_2(g) on the Pt(111) surface leads to the formation of a PtO_2/Pt(111) intermediate that might exist in several forms, shown in Fig. Figure S2. Our data show that PtO_2(g) adsorbed on H site with Pt atom is energetically favored among all calculated structures of PtO_2/Pt(111); the adsorption energy is −2.92 eV.

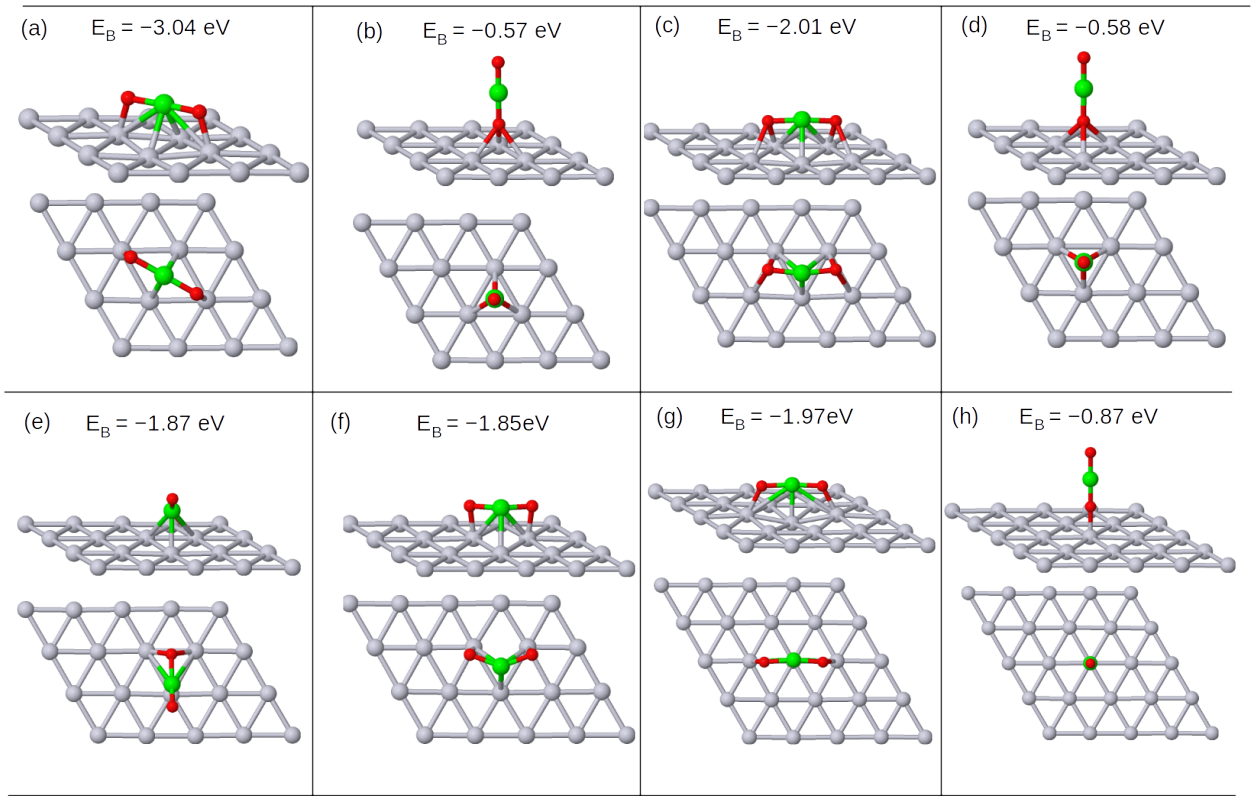

Figure S2: Top and side view of selected stable configurations of isolated PtO_2(g) adsorbed on the Pt(111) surface. In the most stable configuration (a) PtO_2(g) binds with two surface Pt atoms resulting in a binding energy of −2.92 eV. Color scheme: red (O), gray (surface Pt), green (Pt in PtO_2(g)).

SIII Adsorption of PtO_2(g) the Pt(111) step edges

The stepped Pt(533) surface, which consist of 4-atom wide (111) terraces with one (100) step, is modeled by means of periodic supercells comprising 4 layers, with the bottom 2 layer kept fixed in their bulk position, as show in Fig. Figure S3 (a). The lattice dimensions of Pt(533) surfaces are (23.13 Å × 11.22 Å). The adsorption sites on terraces of stepped Pt(533) surface are similar to those seen on the Pt(111) surface, and shown in Fig. Figure S3 (b). Stable configurations of PtO_2(g) adsorbed on stepped Pt(533) surface are shown in Fig. Figure S4.

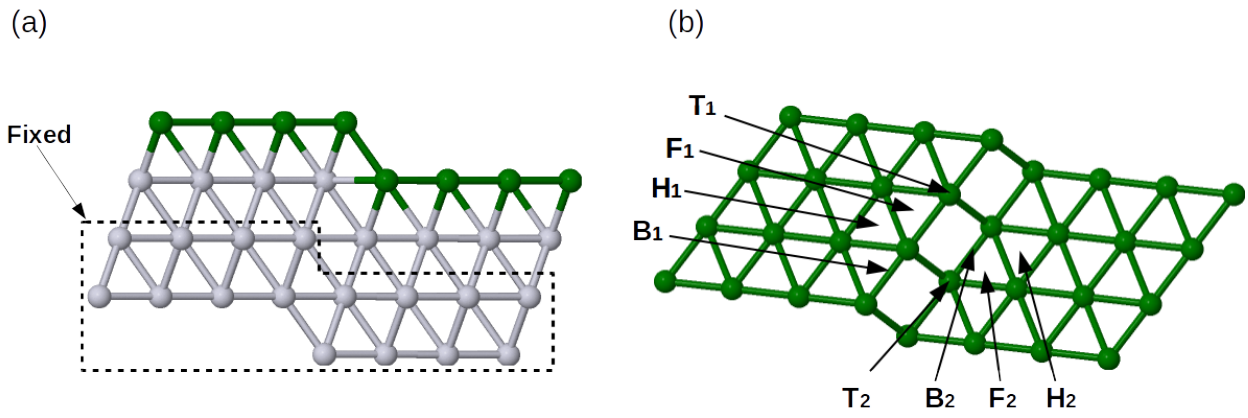

Figure S3: (a) Top and (b) cross-sectional view of structure of stepped Pt(533) surfaces. Surface layer atoms marked green. The adsorption sites are labeled as top (T_1 and T_2), bridge (B_1 and B_2), fcc (F_1 and F_2), and hcp (H_1 and H_2) sites.

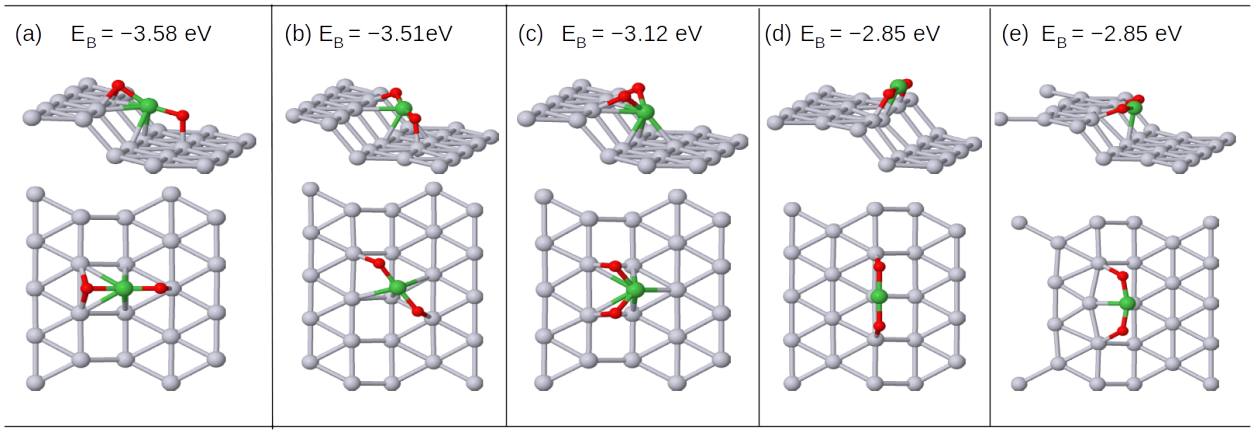

Figure S4: Cross-sectional and top view of selected stable configurations of isolated PtO_2(g) adsorbed on a stepped Pt(533) surface. In the most stable configuration (a) PtO_2(g) binds with the five surface Pt atoms resulting in a binding energy of −3.58 eV. Color scheme: red (O), gray (surface Pt), green (Pt in PtO_2(g)).

SIV PtO_2(g) on flat CeO_2 (111) surfaces

The CeO_2(111) surface is modeled by a p(4 × 4) supercell with three O-Ce-O triple layers and separated by more than 15 Å of vacuum in the direction perpendicular to the surface, as shown in Fig. Figure S5. The bottom two atomic layers are fixed to mimic the bulk, while all other atoms are allowed to relax with the constraint of the fixed supercell sizes. To obtain

the stable adsorption configurations, various adsorption sites for the PtO_2(g) molecule on the CeO_2(111) surface have been considered as shown in Fig. Figure S5(a). The possible adsorption sites include the top sites of a surface 7-fold-coordinated Ce (Ce_{7c}), a surface 3-fold-coordinated O (O_{3c}), and a subsurface 4-fold-coordinated O (O_{4c}), and the bridge sites between them. Stable configurations of PtO_2(g) adsorbed on CeO_2 are shown in Fig. Figure S6.

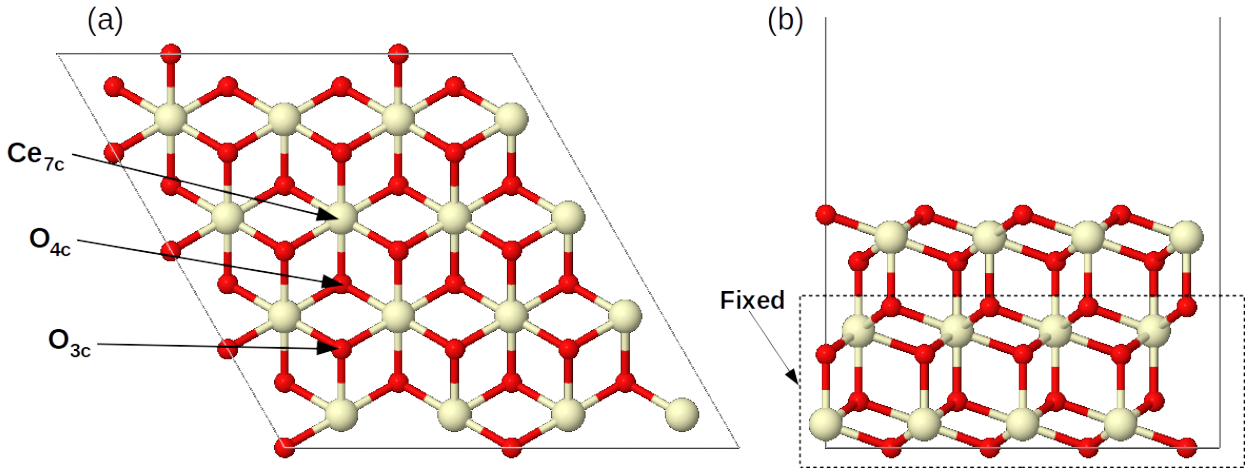

Figure S5: (a) Top and (b) cross-sectional view of CeO_2(111) surface. The adsorption sites include the top sites of a surface 7-fold-coordinated Ce (Ce_{7c}), a surface 3-fold-coordinated O (O_{3c}), and a subsurface 4-fold-coordinated O (O_{4c}). Color scheme: red (O), white (Ce).

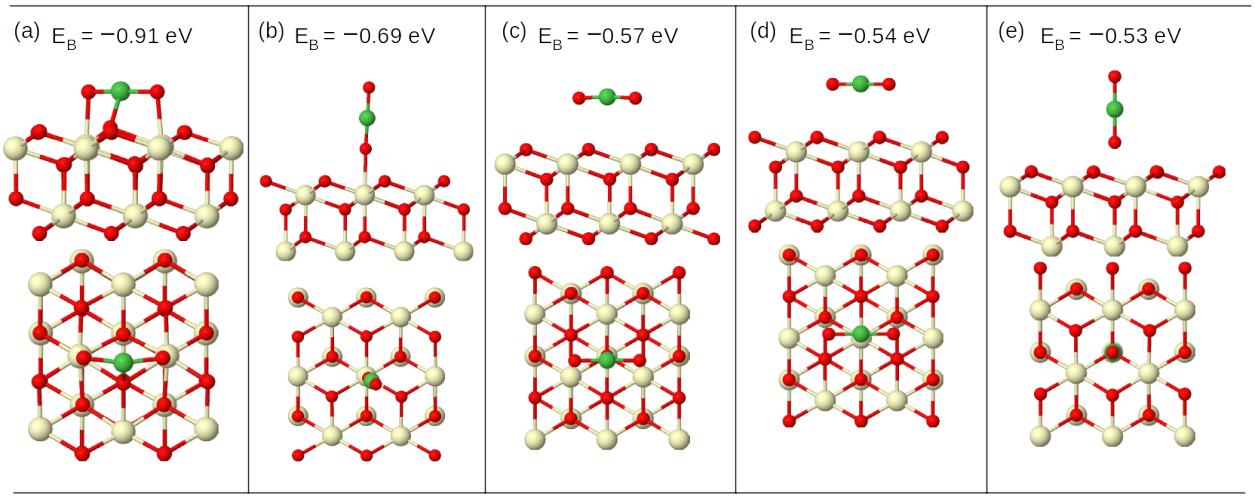

Figure S6: Top and side view of selected stable configurations of isolated PtO_2(g) adsorbed on a CeO_2(111) surface. In the most stable configuration (a) PtO_2(g) binds with the surface O_{3c} atoms resulting in a binding energy of −0.91 eV. Color scheme: red (O), white (Ce), green (Pt).

SV PtO_2(g) on Al_2O_3 (001) surfaces

A 2×1 unit cell (11.19 Å×8.44 Å) of the γ-Al_2O_3(001) surface was simulated using a slab supercell approach, as shown in Fig. Figure S7. There are only 3-fold-coordinated aluminum O_{3c} and 5-fold-coordinated aluminum (Al_{5c}) sites were exposed on the (001) surface, however, there are five non-equivalent Al atoms and 6 non-equivalent O atoms. We investigate PtO_2(g) adsorbed on all those atoms. After relaxing 22 initial structures, the most stable five adsorption configurations are show in Fig. Figure S8.

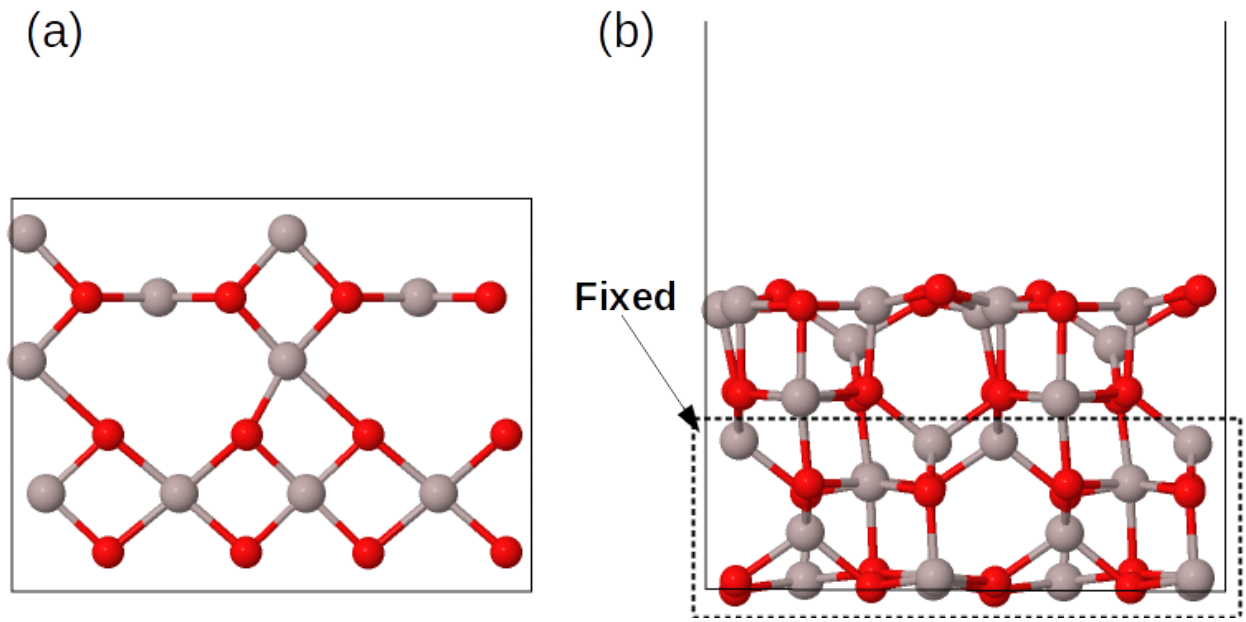

Figure S7: (a) Top and (b) cross-sectional view of Al_2O_3(001) surface. Color scheme: red (O), gray (Al).

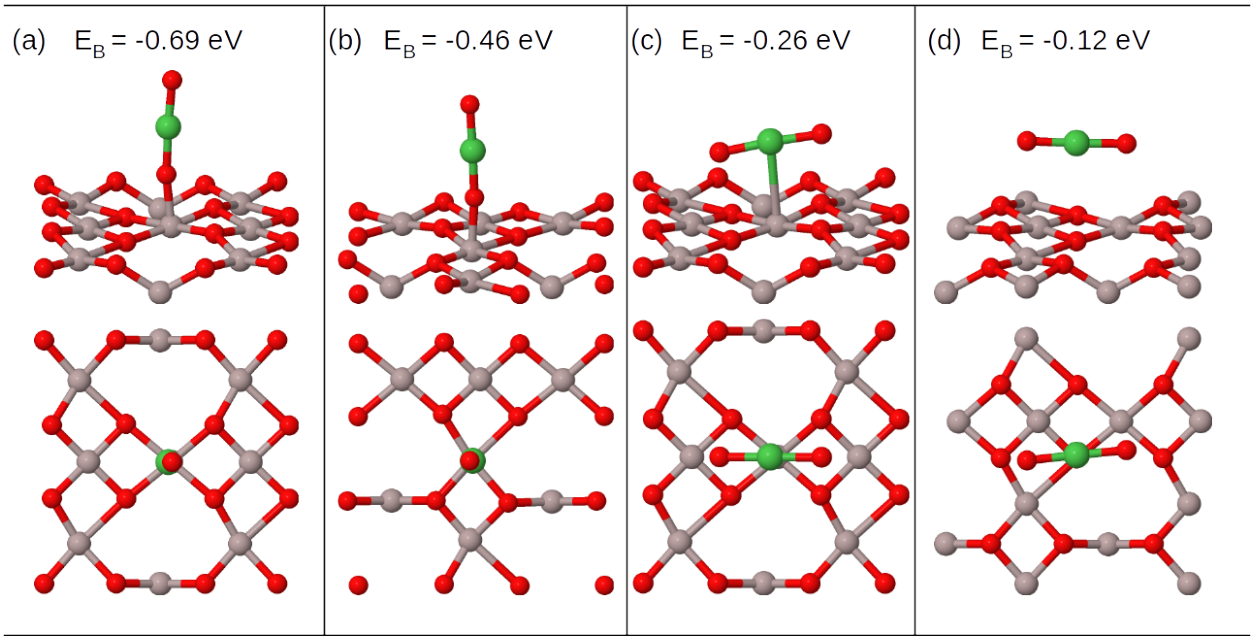

Figure S8: Top and side view of selected stable configurations of isolated PtO_2(g) adsorbed on a Al_2O_3(001) surface. In the most stable configuration (a) PtO_2(g) binds with the surface O_{3c} atom resulting in a binding energy of -0.69 eV. Color scheme: red (O), gray (Al), green (Pt).

SVI Adsorption of PtO_2(g) the CeO_2 (111) step

In the present work, we considered two low-energy monolayer-high steps that we label as step I and step II following Ref. 32. The edge of both step I and step II are oriented along the [110] direction. These surface steps were modeled with periodic slabs separated by > 15Å of vacuum in the direction perpendicular to the (111) terrace. The dimensions of the cells were 17.97 Å×11.67 Å^2 along the [112] and [110] directions (step I) and 15.72 Å×11.67 Å^2 along the [112] and [110] (step II), as shown in Fig. Figure S9. The adsorption sites on stepped CeO_2 step surface are similar to those seen on the CeO_2 (111) surface, where PtO_2(g) can adsorb on the Ce_{7c}, a surface O_{3c}, and O_{4c}, and the bridge sites between them. Stable configurations of PtO_2(g) adsorbed on CeO_2 are shown in Fig. Figure S10.

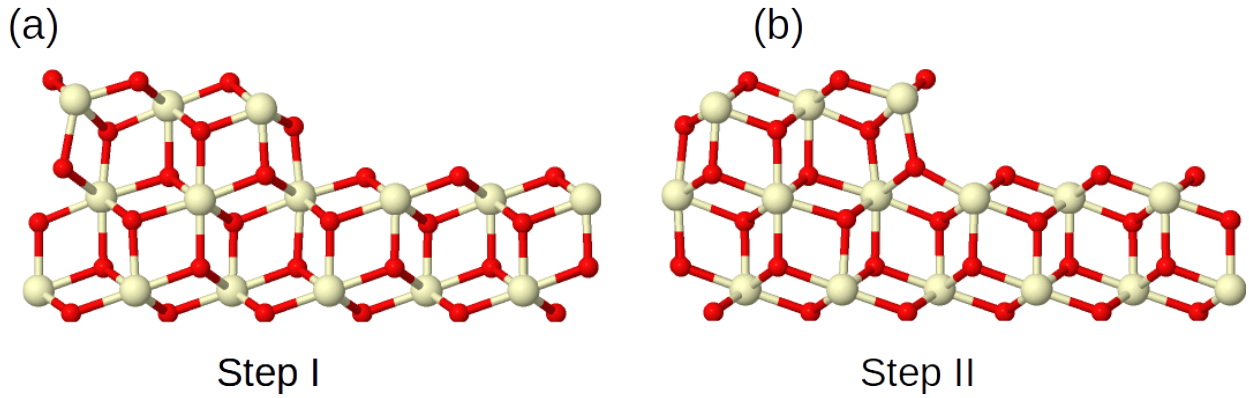

Figure S9: Side view of stepped CeO_2 surface. (a) Step I display down-sloping O−O units perpendicular to the edge direction; (b) Step II display a concave shape with the outermost atom row being an O-row in the topmost atomic plane. Color scheme: red (O), white (Ce).

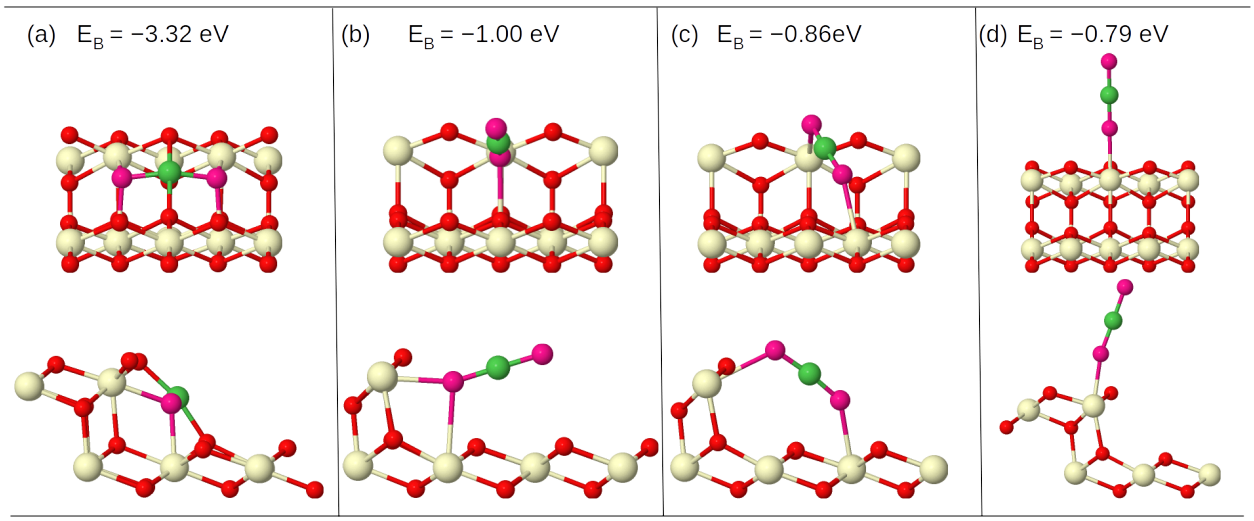

Figure S10: Top and side view of selected stable configurations of isolated PtO_2(g) adsorbed on the stepped CeO_2 surface. In the most stable configuration (a) PtO_2(g) forms a square-planar unit [PtO_4] with the two surface O atoms resulting in a binding energy of −3.32 eV. Color scheme: red (surface O), white (Ce), green (Pt), peak (oxygen in PtO_2(g)) and light peak (adsorbed oxygen).

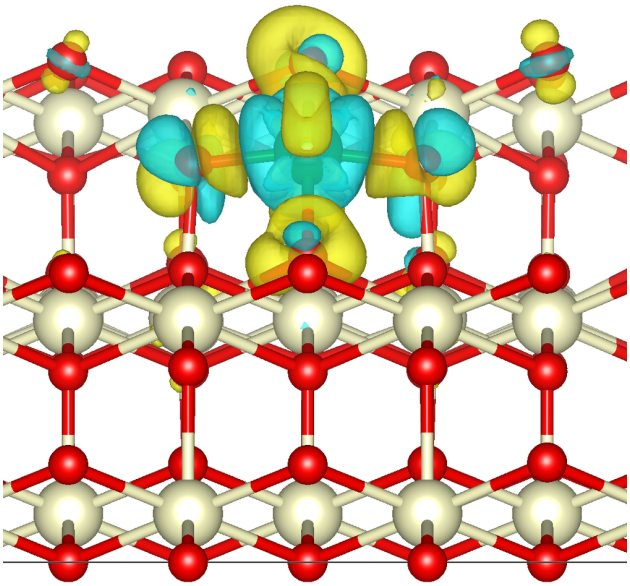

Figure S11: Charge density difference map of the adsorption state of single platinum atom on the $[PtO_4]/CeO_2$ stepped (111) surface, yellow color represents for electron accumulation while light-blue for electron depletion.