Supplementary Information

A DFT+U revisit on reconstructed CeO$_2$(100) surfaces: structures, thermostabilities and reactivities

Chong-Yuan Zhou, Dong Wang and Xue-Qing Gong*

Key Laboratory for Advanced Materials, Centre for Computational Chemistry and Research Institute of Industrial

Catalysis, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130

Meilong Road, Shanghai 200237, P.R. China
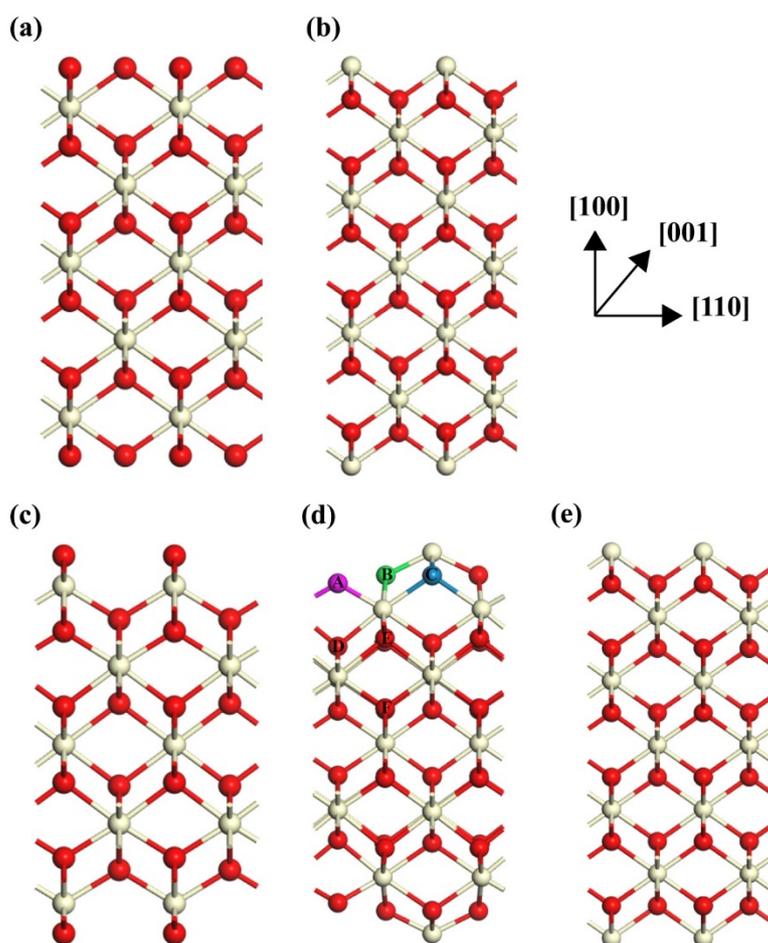
Figure S1 Structures of the intact (a, b) and reconstructed (c-e) CeO$_2$(100) surfaces from the side views. (a) Intact CeO$_2$(100) with a full layer of surface O; (b) intact CeO$_2$(100) with a full layer of surface Ce; (c) reconstructed O-t surface with a half-layer of surface O; (d) reconstructed CeO$_4$-t surface modeled by introducing CeO$_2$ units onto the O-t surface; (e) reconstructed Ce-t surface with a half-layer of surface Ce.
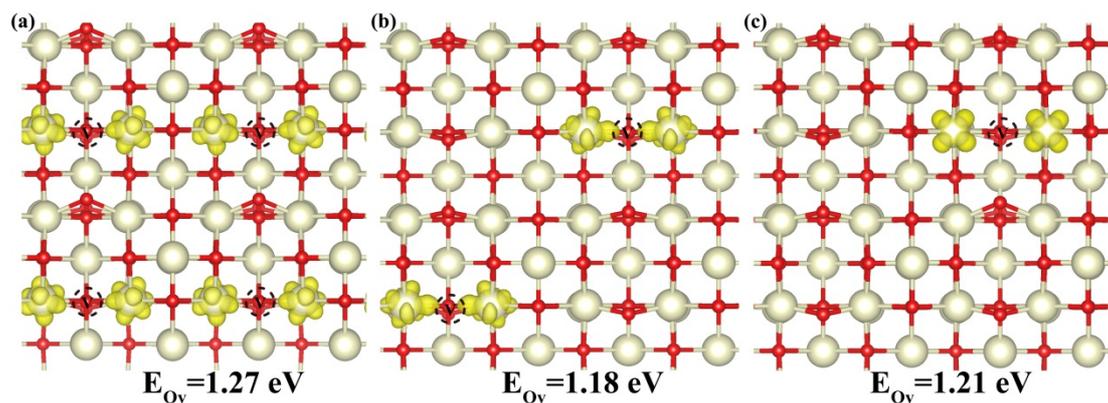
Figure S2 Calculated spin charge plots and average E_{Ov} values (per O_v) of O_v at the O^A site on the CeO$_4$-t surface using a $p(4\times4)$ model at the O_v concentration of (a) 100%, (b) 50%, and (c) 25%, respectively.
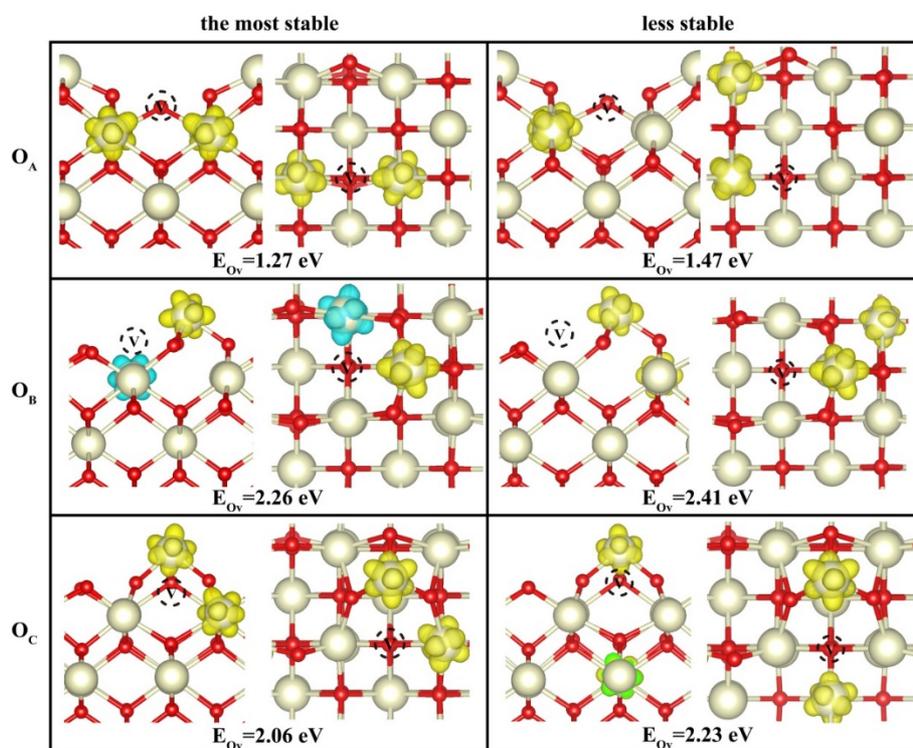
Figure S3 Calculated spin charge plots (side and top views) of the reduced CeO$_4$-t surfaces with the O_v at the (top row) O^A, (middle) O^B and (bottom) O^C sites, respectively, with both the most and less stable electronic configurations for the distributions of the localized electrons.

(a)   **(b)**   **(c)**   **(d)**   **(e)**

E_0 $\Delta E = 0.18$ eV $\Delta E = 0.22$ eV $\Delta E = 0.13$ eV $\Delta E = 0.06$ eV
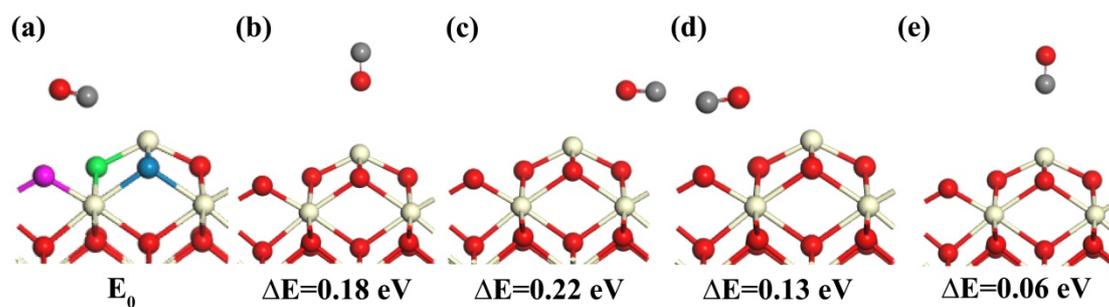
Figure S4 Calculated structures and relative energies of CO adsorption on the CeO_4-t surface. The calculated adsorption energy for CO at O^B (a) is 0.28 eV and it is taken as the reference.

(a)   **(b)**   **(c)**

$E_b = 0.27$ eV $E_b = 0.51$ eV $E_b = 0.32$ eV
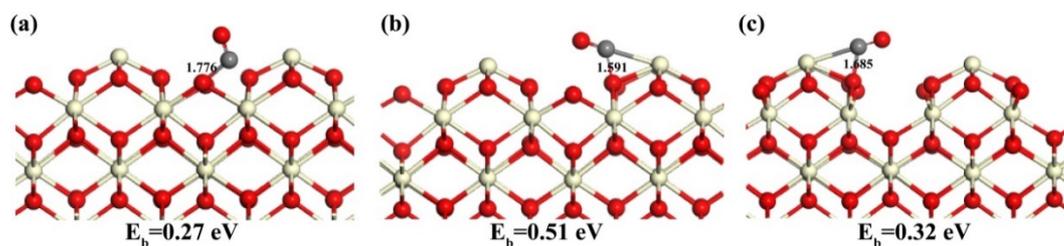
Figure S5 Calculated structures of transition states of CO oxidation via the channel of the (a) O^A, (b) O^B and (c) O^C on the CeO_4-t surface using a $p(4 \times 4)$ model. The corresponding reaction barriers are also listed.

(a)   **(b)**
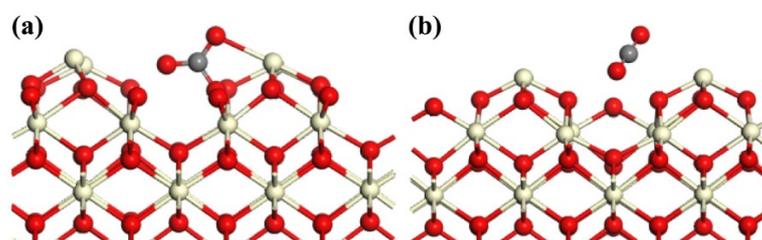
Figure S6 Calculated structures of the (a) carbonates species formed via the O^C channel and (b) the linear CO_2 via the O^A channel using a $p(4 \times 4)$ model.

(a)　(b)　(c)　(d)

E_{ads}=1.59 eV　E_{ads}=2.34 eV　E_{ads}=1.86 eV　E_{ads}=1.93 eV
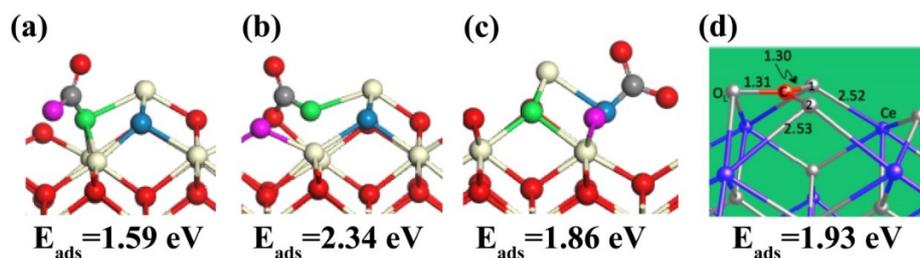
Figure S7 Calculated formation energies and structures of the carbonate species on (a-c) the CeO_4-t type of reconstructed CeO_2(100) from our work and (d) on the CeO_2(100) surface reported by Mullins and co-workers. (ref. 39 in the main text).

CO adsorption　TS　CO_2　carbonate

E=-0.28 eV　E=0.01 eV　E=-2.25 eV　E=-3.58 eV

E=-0.26 eV　E=-0.20 eV　E=-1.56 eV　E=-2.60 eV
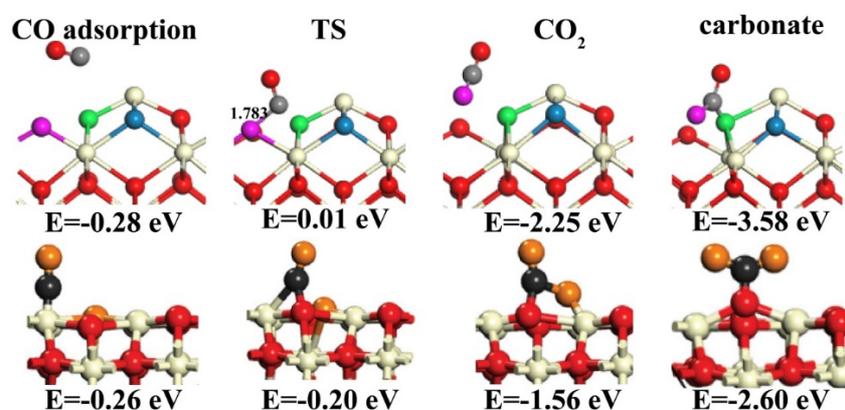
Figure S8 Calculated structures and energetics of CO oxidation from our results on the CeO_4-t surface (top row) and the corresponding reverse processes of CO_2 reduction on the defective CeO_2(110) reported by Lo and co-workers (bottom row; ref. 40 in the main text).