Supplementary Information

Clarifying the Impacts of Surface Hydroxyls on CO Oxidation on the $CeO_2(100)$ Surfaces: A DFT+U Study

Hui 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
*E-mail: wangd@ecust.edu.cn; xgong@ecust.edu.cn

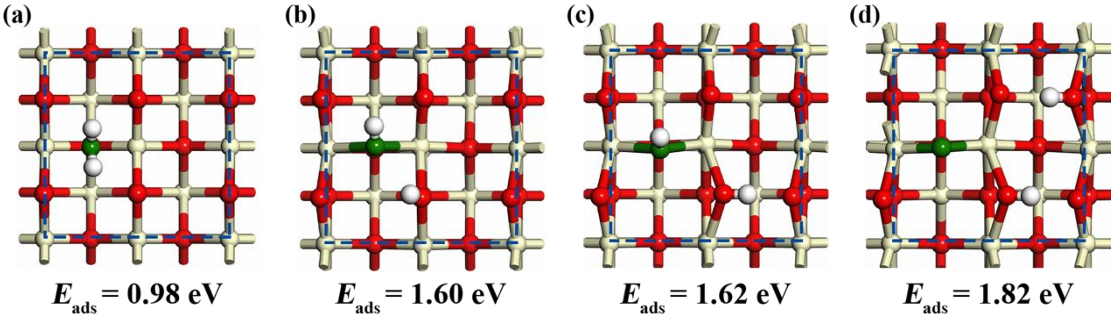

Figure S1. Calculated structures and adsorption energies of H_2O on the O-t $CeO_2(100)$ surface.

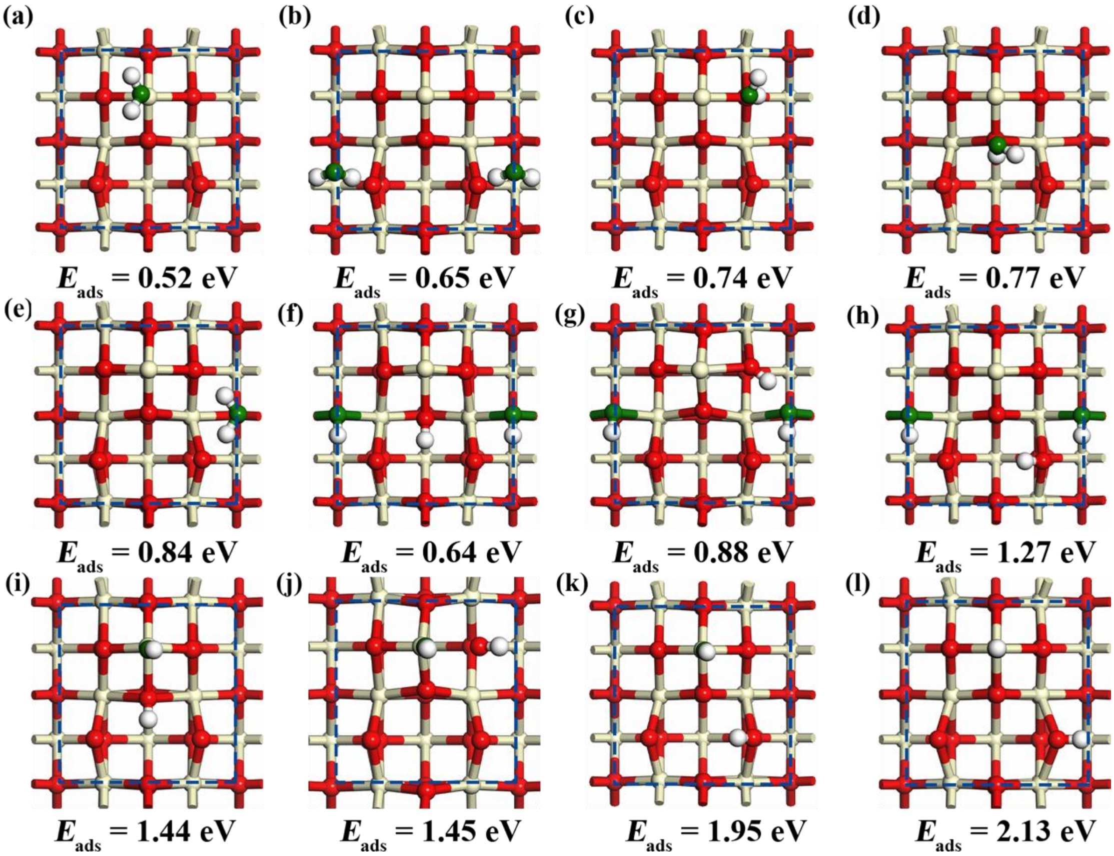

Figure S2. Calculated structures and adsorption energies of H_2O on the CeO_4-t CeO_2(100) surface.

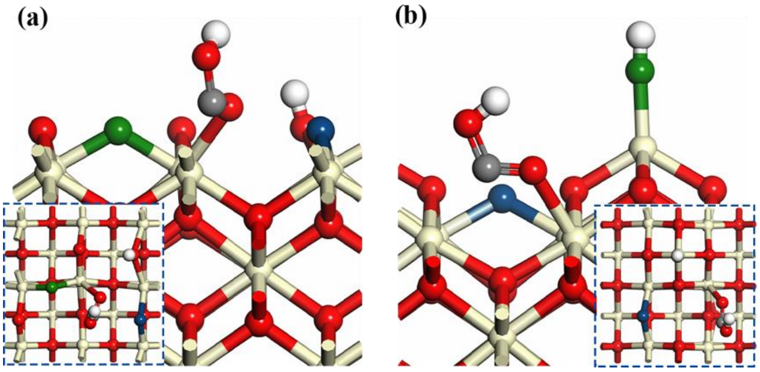

Figure S3. Side views of the calculated structures of adsorbed carboxyl (COOH) on the hydroxylated O-t (a) and CeO_4-t (b) surfaces, where the corresponding top views are also given in the inset.

Table S1. Calculated formation energies of the carboxyl (COOH) species relative to the adsorbed CO on the hydroxylated O-t and CeO_4-t surfaces. Negative E_{form} values indicate that the formation of COOH is endothermic.

Items	E_{ads}(CO) / eV	E_{form}(COOH) / eV	Structure
O-t	0.42	-0.71	Figure S3a
CeO_4-t	0.06	-0.46	Figure S3b

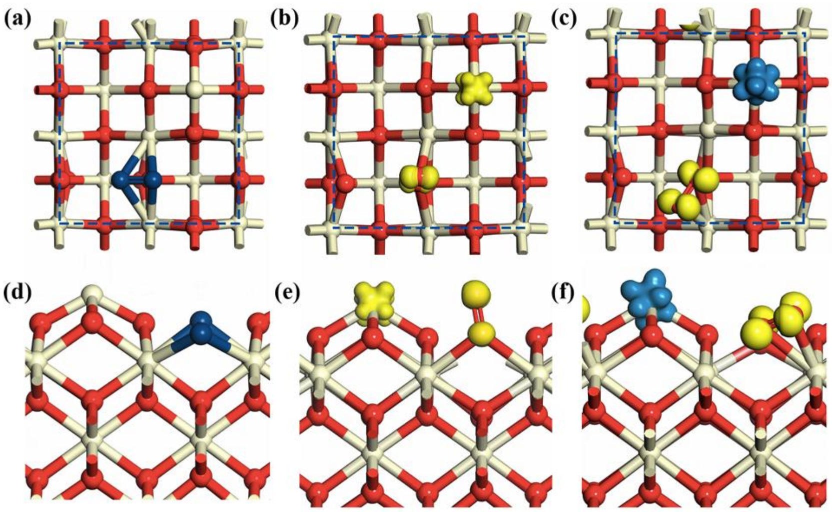

Figure S4. Calculated spin-polarized charge densities (top and side views) of the peroxide (a, d) and superoxide species (b, e for the end-on while c, f for the side-on configuration) being adsorbed at the O_v site on the CeO$_4$-t surface. Spin-up and down densities are colored in yellow and blue at the iso-surface of 0.01 |e|/Bohr^3.

Table S2. Calculated adsorption energies (E_{ads}), Bader charges, and O-O bond lengths of the peroxide (O_2^{2-}) or superoxide (O_2^-) species being adsorbed at the O_v site on the CeO$_4$-t surface. Positive E_{ads} values indicate exothermic O_2 adsorption processes.

Species	E_{ads} / eV	Bader charge / |e|	O-O bond length / Å
peroxide (O_2^{2-})	0.87	-1.173	1.455
superoxide (O_2^-, end-on)	0.58	-0.689	1.325
superoxide (O_2^-, side-on)	0.86	-0.699	1.335

As seen in Figure S4 and Table S2, we calculated and compared the adsorption energies, Bader charges, O-O bond lengths, and spin-polarized charge densities, about the adsorbed superoxide and peroxide species on the CeO$_4$-t surface. It was found that, i) the peroxide O_2^{2-} favors to anchor at the O_v site via both of O atoms (Figure S4a), forming a side-on geometry with elongated O-O bond length of 1.455 Å; ii) the superoxide O_2^- has two adsorption configurations of the end-on (Figure S4e) and side-on (Figure S4f) structures depending on the number of O involved in binding the vacancy, and the latter is thermodynamically more stable, albeit their comparable O-O bond lengths.

Since the calculated adsorption energies (0.87 vs. 0.86 eV; Table S2) and structures (side-on configuration) are quite similar for the peroxide and superoxide species, it is seemingly difficult to control these two types of adsorption on the CeO$_4$-t surface. However, spin-polarized charge density analysis in Figure S4 shows that the key for the

O_2^{2-}/O_2^- formation lies in whether the second electron is captured by the pre-formed O_2^- (i.e. the peroxide pathway) or by a surface protruding Ce$_{4c}$ cation (i.e. the superoxide pathway). This was further confirmed from calculated Bader charges in Table S2. Therefore, our results indicate a possible strategy to alter the peroxide/superoxide formation by suppressing/promoting the ability of surface Ce$_{4c}$ in trapping electrons.

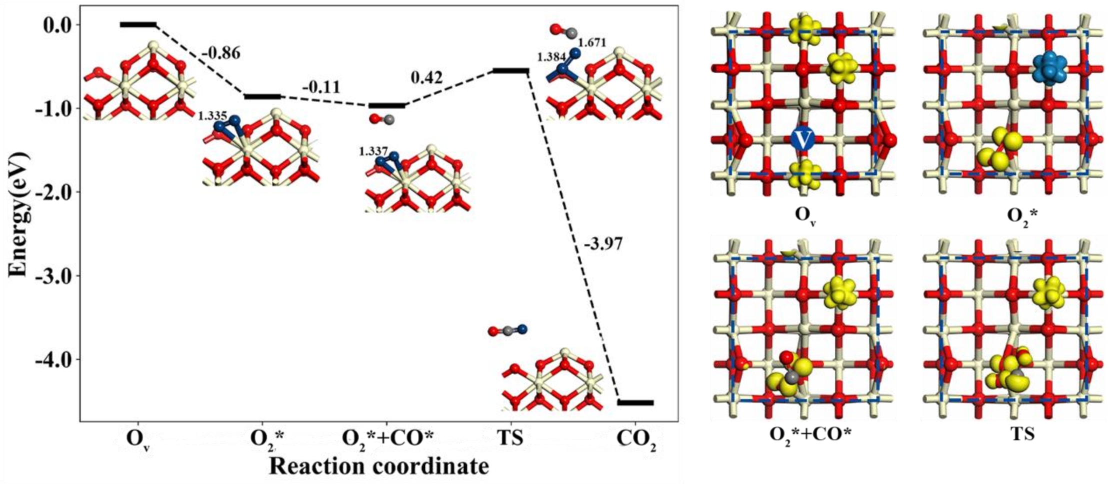

Figure S5. Calculated energy profile and key structures of CO oxidation in the stage II via the superoxide O_2^- pathway. The corresponding electronic structures (localized electrons) of the key intermediates are also presented. Unit of bond distance: Å.