Supplemental Information for:

Catalytic Propane Reforming Mechanism over Zr-Doped CeO_2 (111)

*Matthew D. Krcha, Michael J. Janik**

Department of Chemical Engineering, Pennsylvania State University, University Park, PA 16802

Information available:

Figures S14. Structures for hydrogen adsorption on a CeO_2 (111) surface with 2 and 3 oxygen vacancies.

Figures S15. Structures for hydrogen adsorption on a CeO_2 (111) surface with 4, 5 and 6 oxygen vacancies.

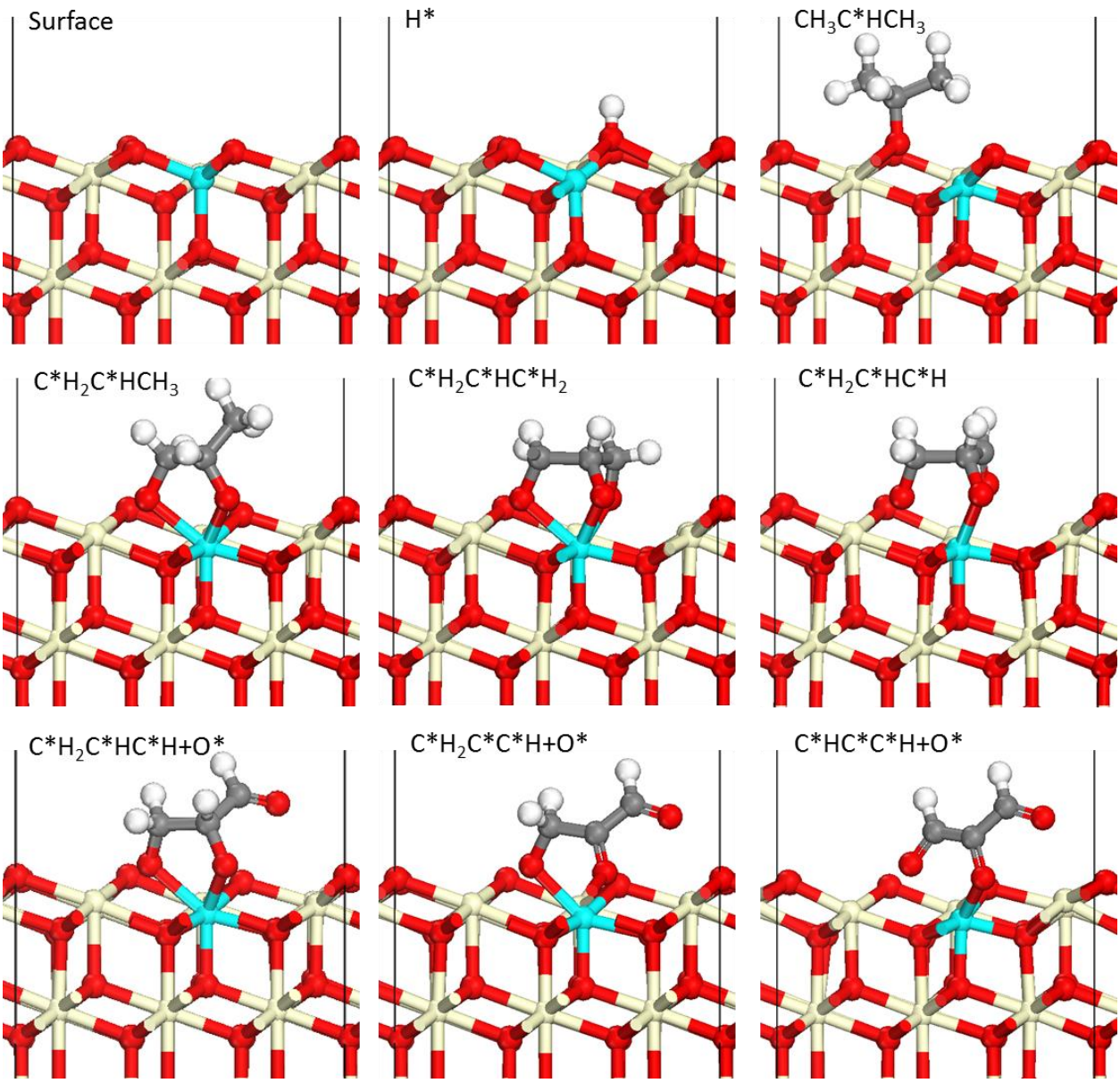

Figure S1. Structures for first 9 steps (excluding desorption of H* as H_2O and refilling of the ½ V_O) to reform propane in an oxidizing environment. Ce is displayed as tan (light), Zr as light blue (gray), O as red (dark).

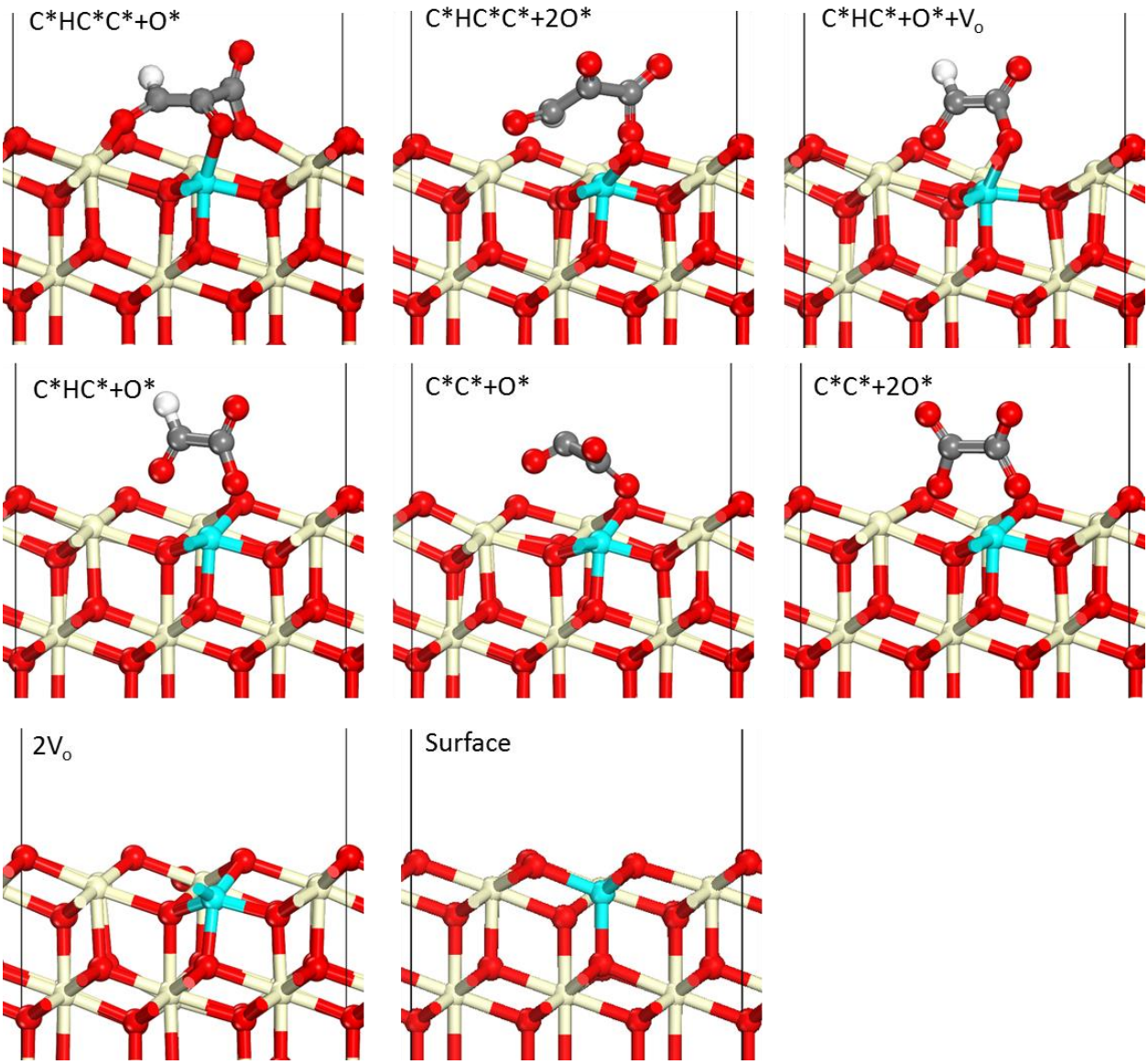

Figure S2. Structures for last 8 steps (excluding desorption of H* as H_2O and refilling of the ½ V_O) to reform propane in an oxidizing environment. Ce is displayed as tan (light), Zr as light blue (gray), O as red (dark).

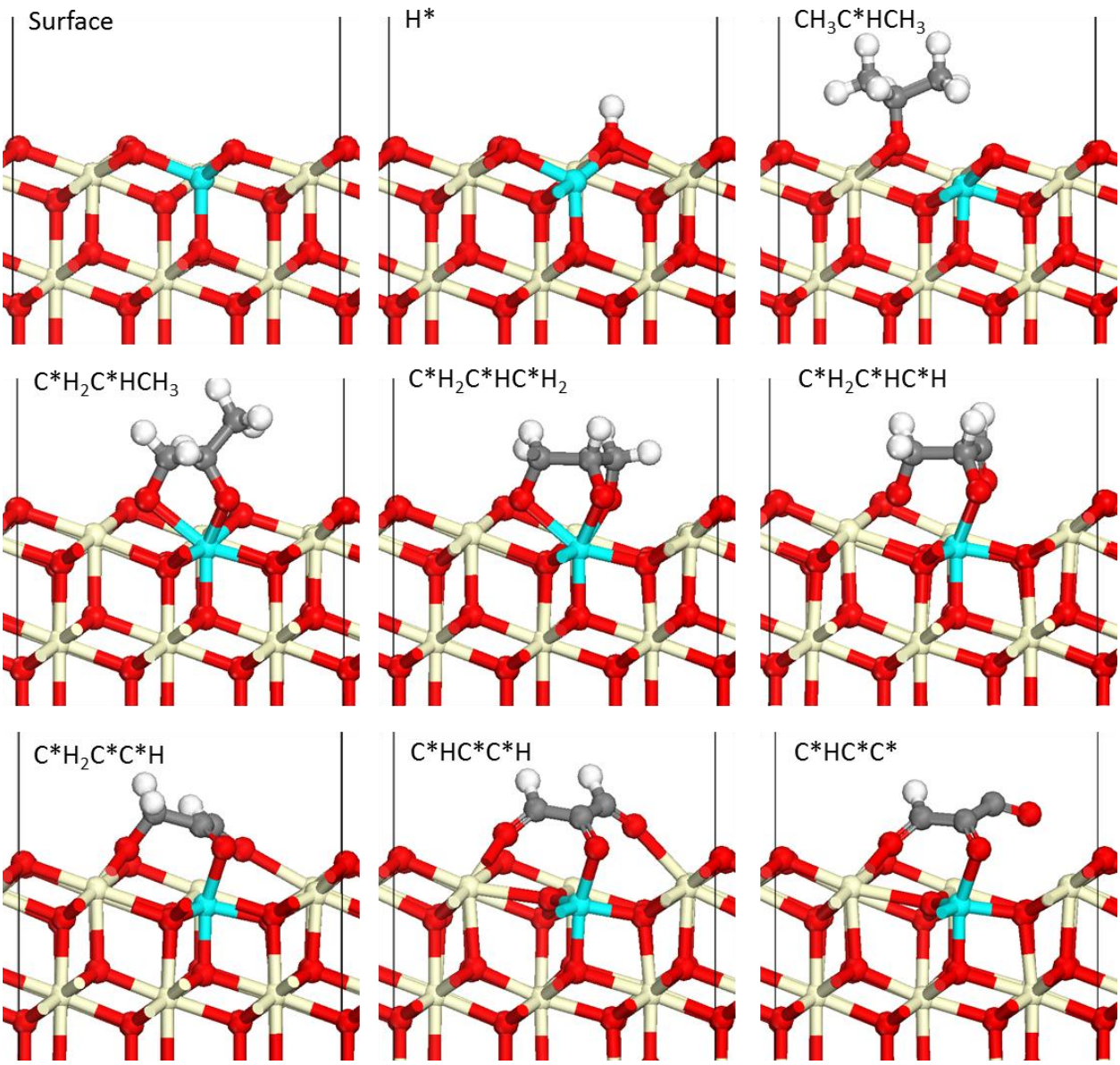

Figure S3. Structures for first 9 steps (excluding desorption of H* as H_2O and refilling of the ½ V_O) to reform propane in a reducing environment. Ce is displayed as tan (light), Zr as light blue (gray), O as red (dark).

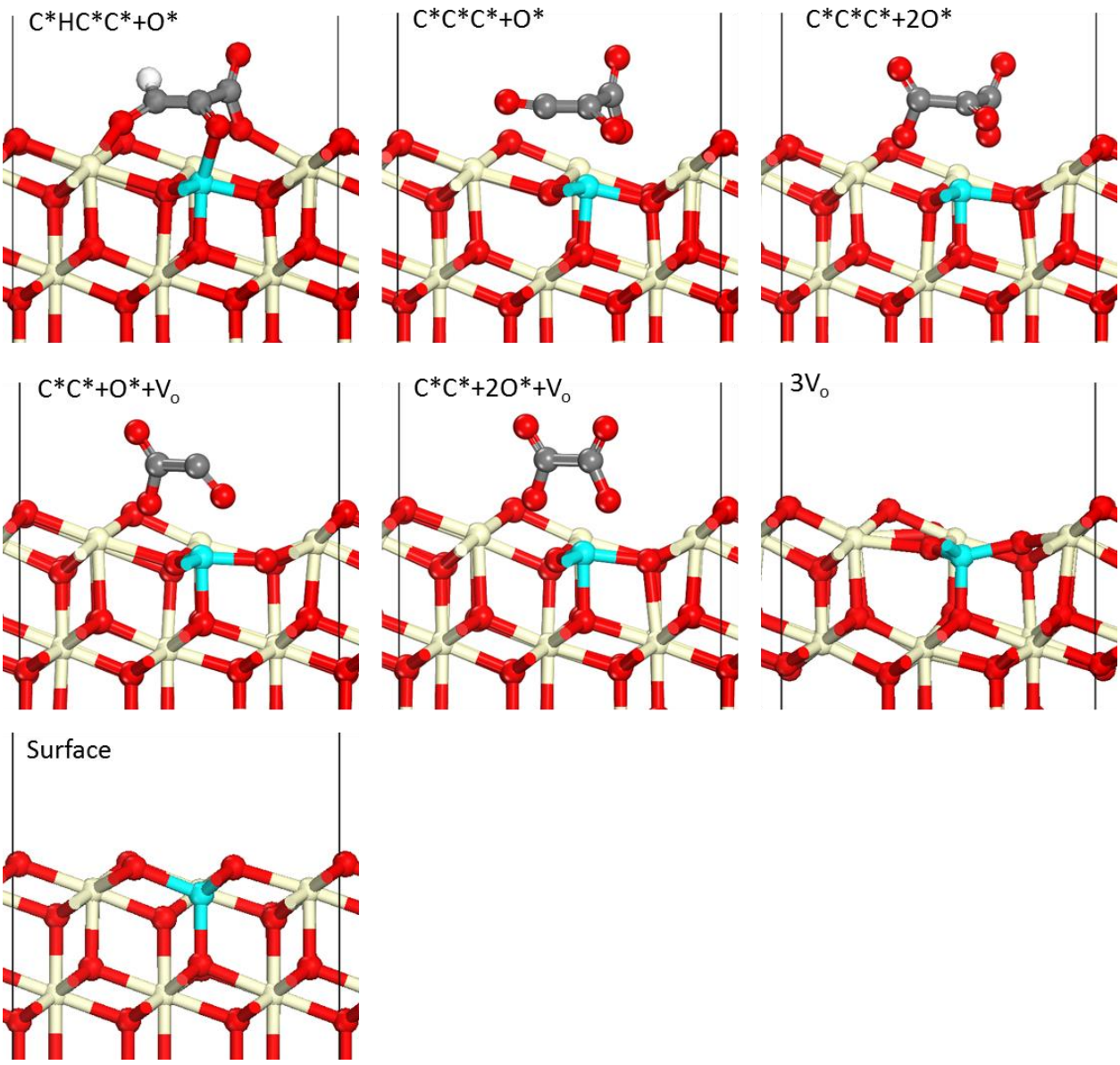

Figure S4. Structures for last 7 steps (excluding desorption of H* as H_2O and refilling of the ½ V_O) to reform propane in a reducing environment. Ce is displayed as tan (light), Zr as light blue (gray), O as red (dark).

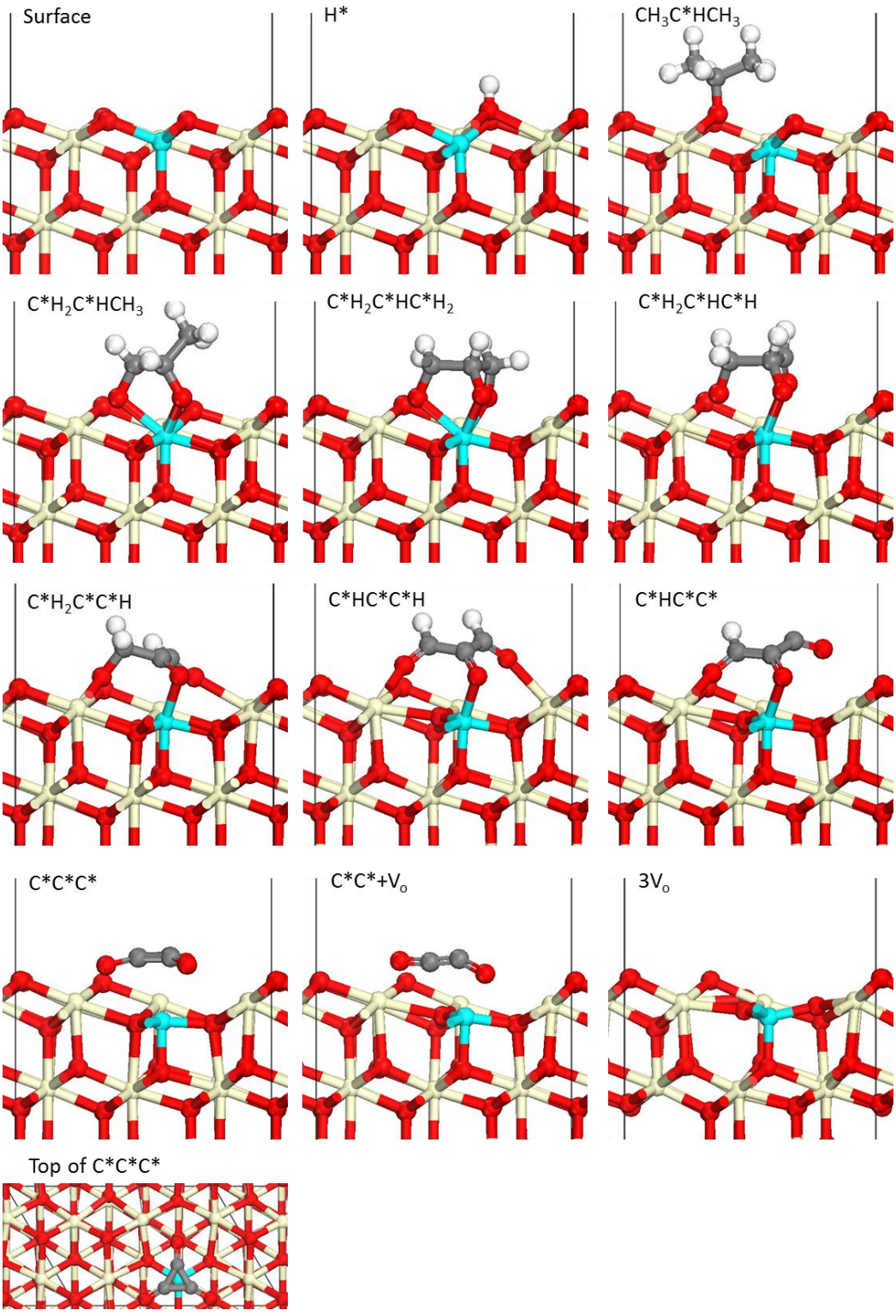

Figure S5. Structures for all of the steps (excluding desorption of H* as H_2O and refilling of the ½ V_O) to reform propane under extremely reducing (gasifier effluent) conditions. Ce is displayed as tan (light), Zr as light blue (gray), O as red (dark).

Number of Oxygen Vacancies	Pure CeO_2 (eV)	Zr-doped CeO_2 (eV)
1	2.57	1.86
2	2.59	1.69
3	2.73	2.74
4	2.34	2.39
5	2.56	3.07
6	2.63	-

Table S1. 0 K oxygen vacancy formation energies for pure CeO_2 (111) and Zr-doped CeO_2 (111). Each successive oxygen vacancy formation energy is calculated relative to a surface with one less vacancy. The 6^{th} oxygen vacancy in Zr-doped CeO_2 is not electronically possible due the number of cerium atoms that would have to reduce, see Section 3.4.

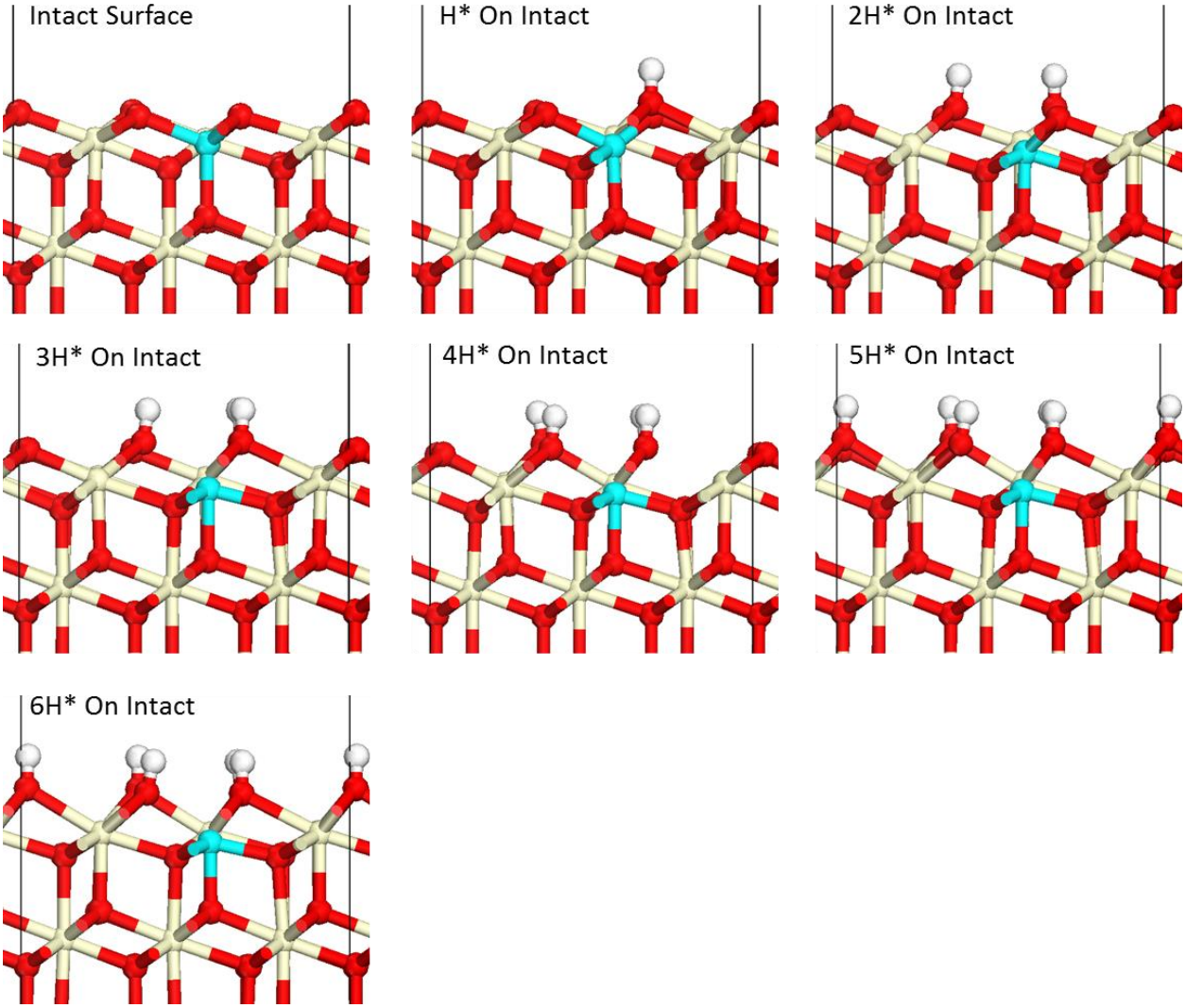

Figure S6. Structures for hydrogen adsorption on an intact Zr-doped CeO_2 surface. Ce is displayed as tan (light), Zr as light blue (gray), O as red (dark).

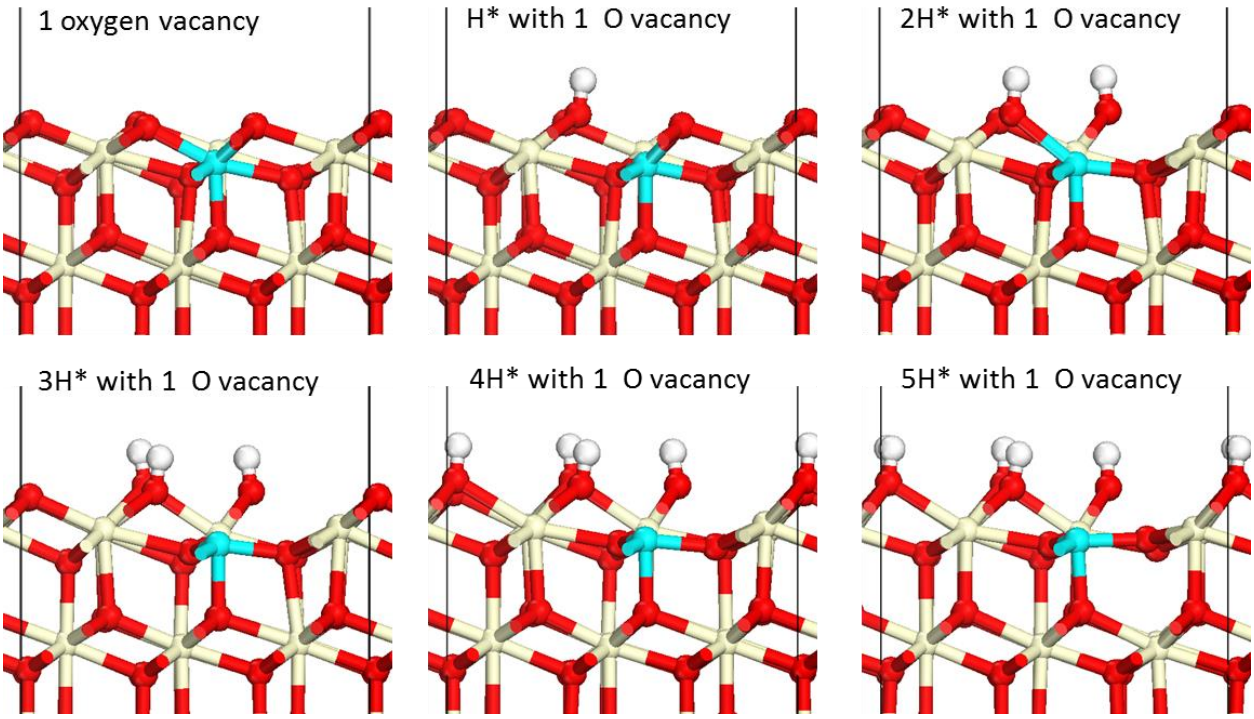

Figure S7. Structures for hydrogen adsorption on a Zr-doped CeO_2 surface with 1 oxygen vacancy. Ce is displayed as tan (light), Zr as light blue (gray), O as red (dark).

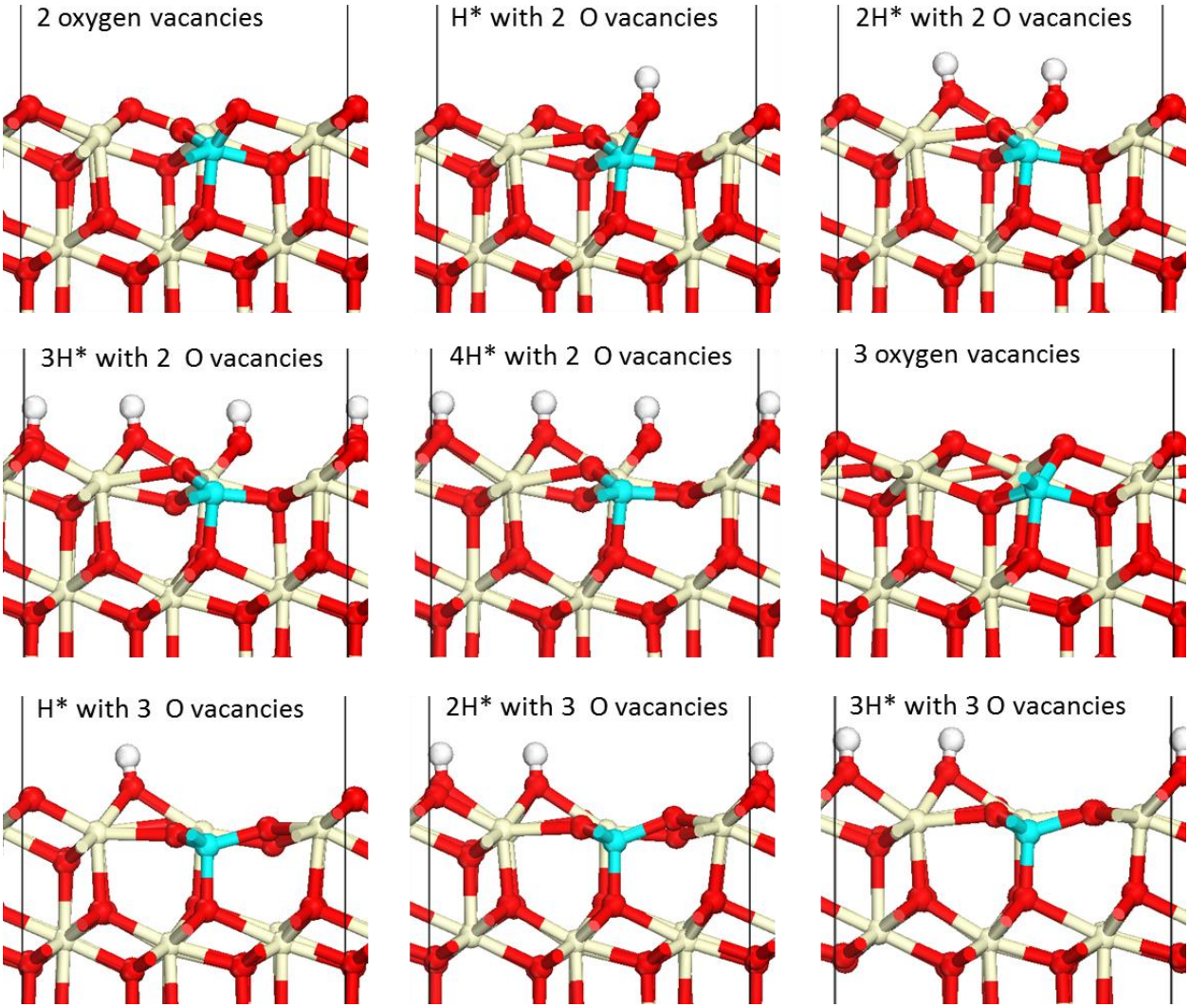

Figure S8. Structures for hydrogen adsorption on a Zr-doped CeO_2 surface with 2 and 3 oxygen vacancy. Ce is displayed as tan (light), Zr as light blue (gray), O as red (dark).

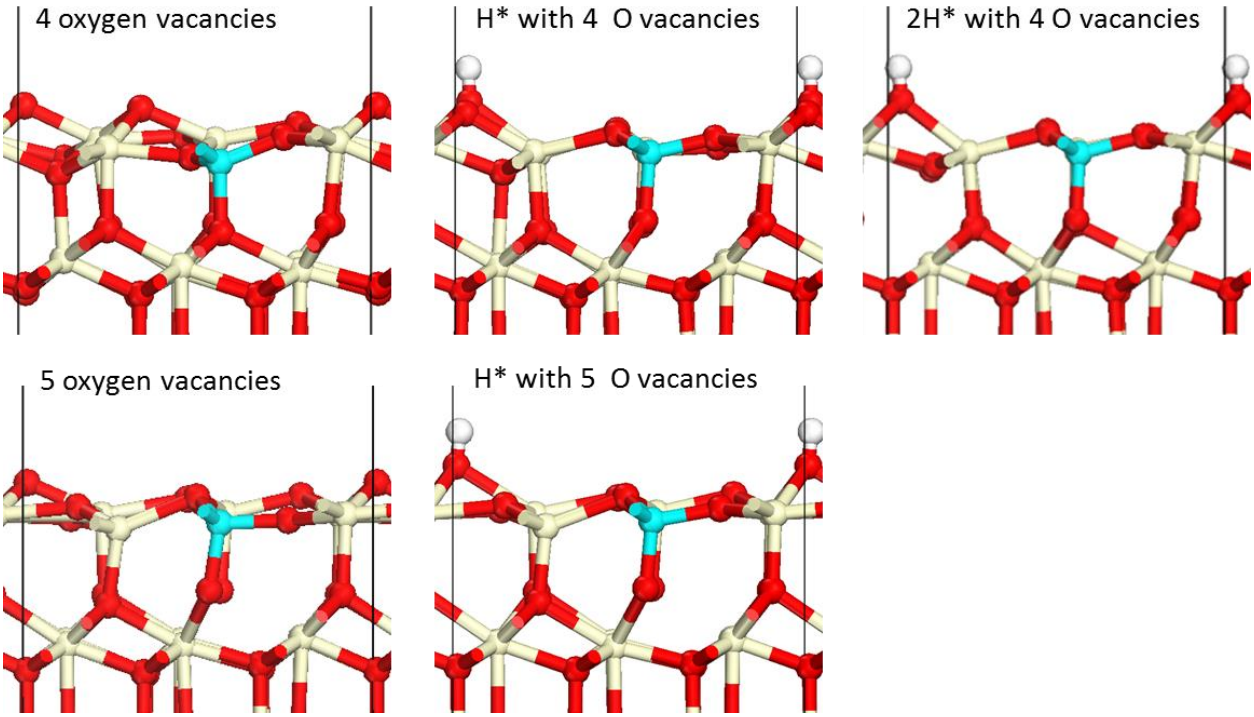

Figure S9. Structures for hydrogen adsorption on a Zr-doped CeO_2 surface with 4 and 5 oxygen vacancy. Ce is displayed as tan (light), Zr as light blue (gray), O as red (dark).

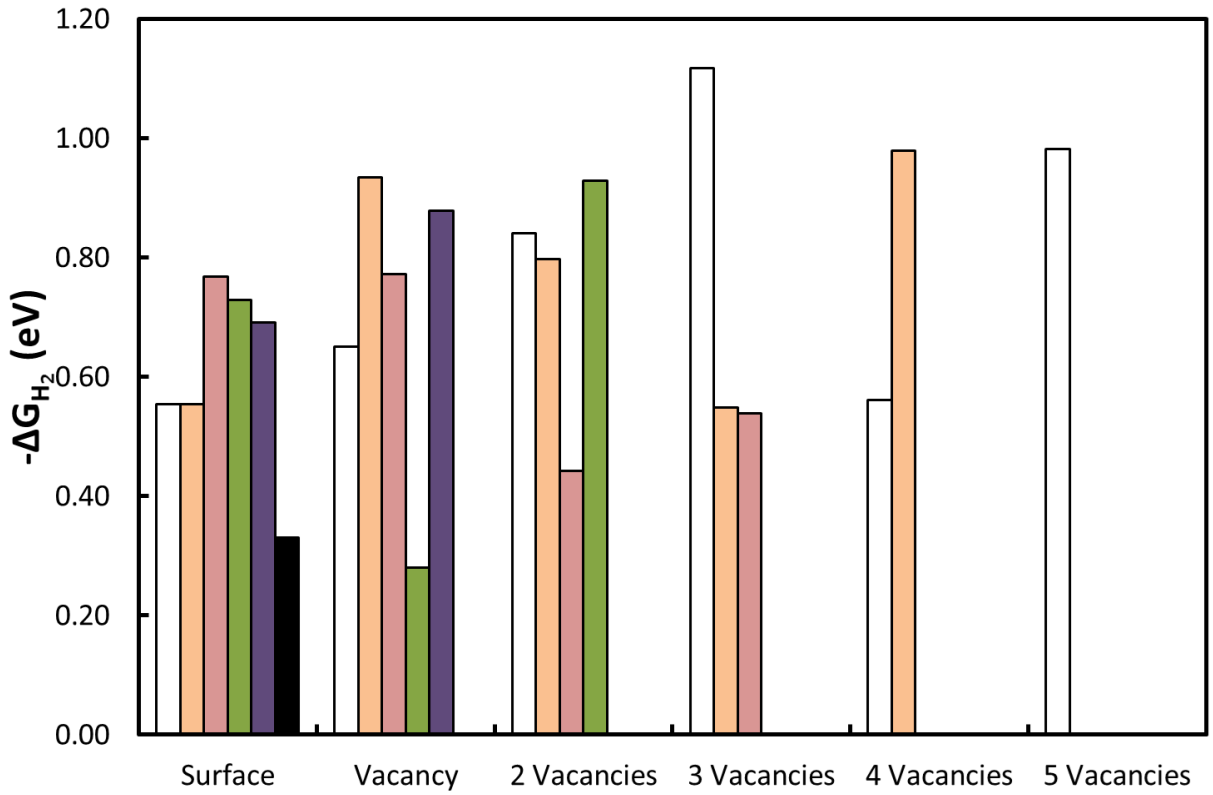

Figure S10. The energy to absorb ½ H_2 (g) onto the surface of pure CeO_2 varying number of surface oxygen vacancies and number of hydrogen atoms on the surface. The energy to absorb each hydrogen atom is calculated progressively in each step. The partial pressure of hydrogen is 0.234 atm and for oxygen is $6x10^{-20}$ atm. (white) 1 hydrogens, (orange or lightest gray) 2 hydrogens, (red or light gray) 3 hydrogens, (green or medium gray) 4 hydrogens, (purple or dark gray) 5 hydrogens, (black) 6 hydrogens.

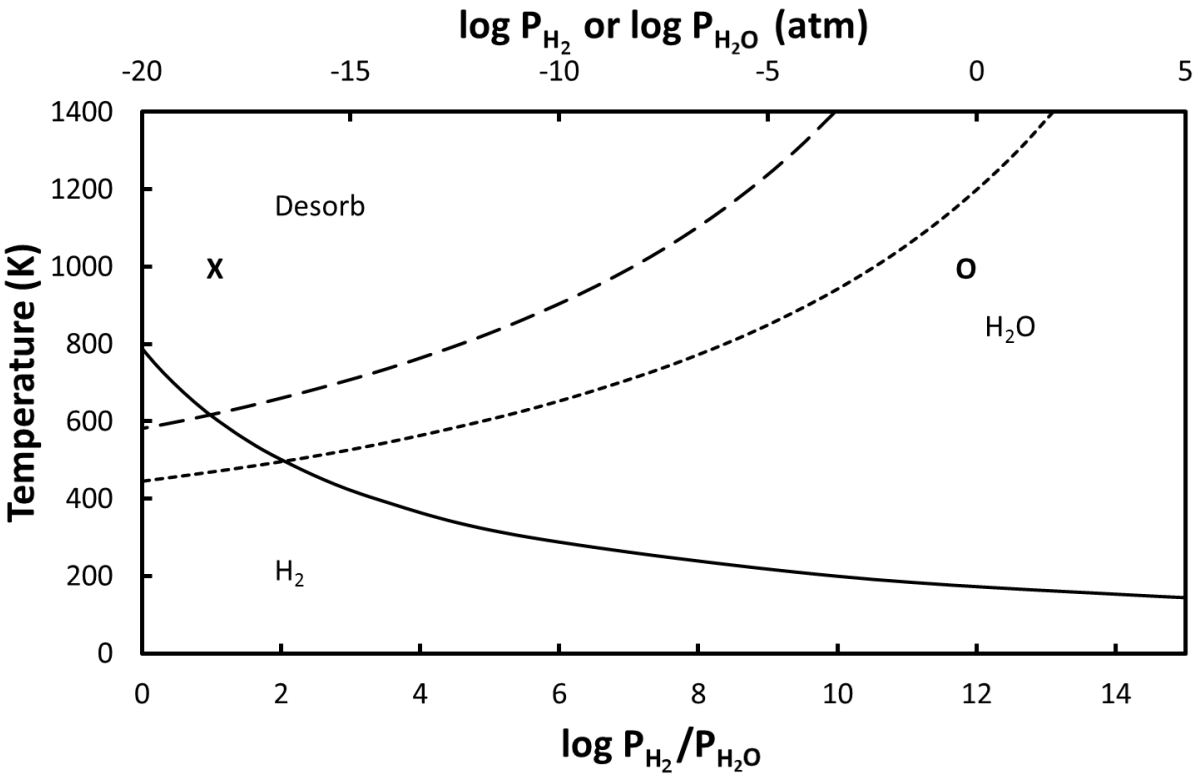

Figure S11. The pressure-temperature curves as to whether the hydrogen on the surface of pure ceria will desorb as H_2 or H_2O for a pure ceria surface with 6 hydrogens. (——) the division between whether the hydrogen will desorb as H_2 (lower) or H_2O (upper) based on the lower axes. The division on whether the hydrogen will desorb as (– –) H_2, or (------) H_2O, upper axes. Above these lines the hydrogen will desorb and below they will not. The X's represent the composition of the gas when the H_2 or H_2O will desorb and the O's represent the conditions if the hydrogen will desorb.

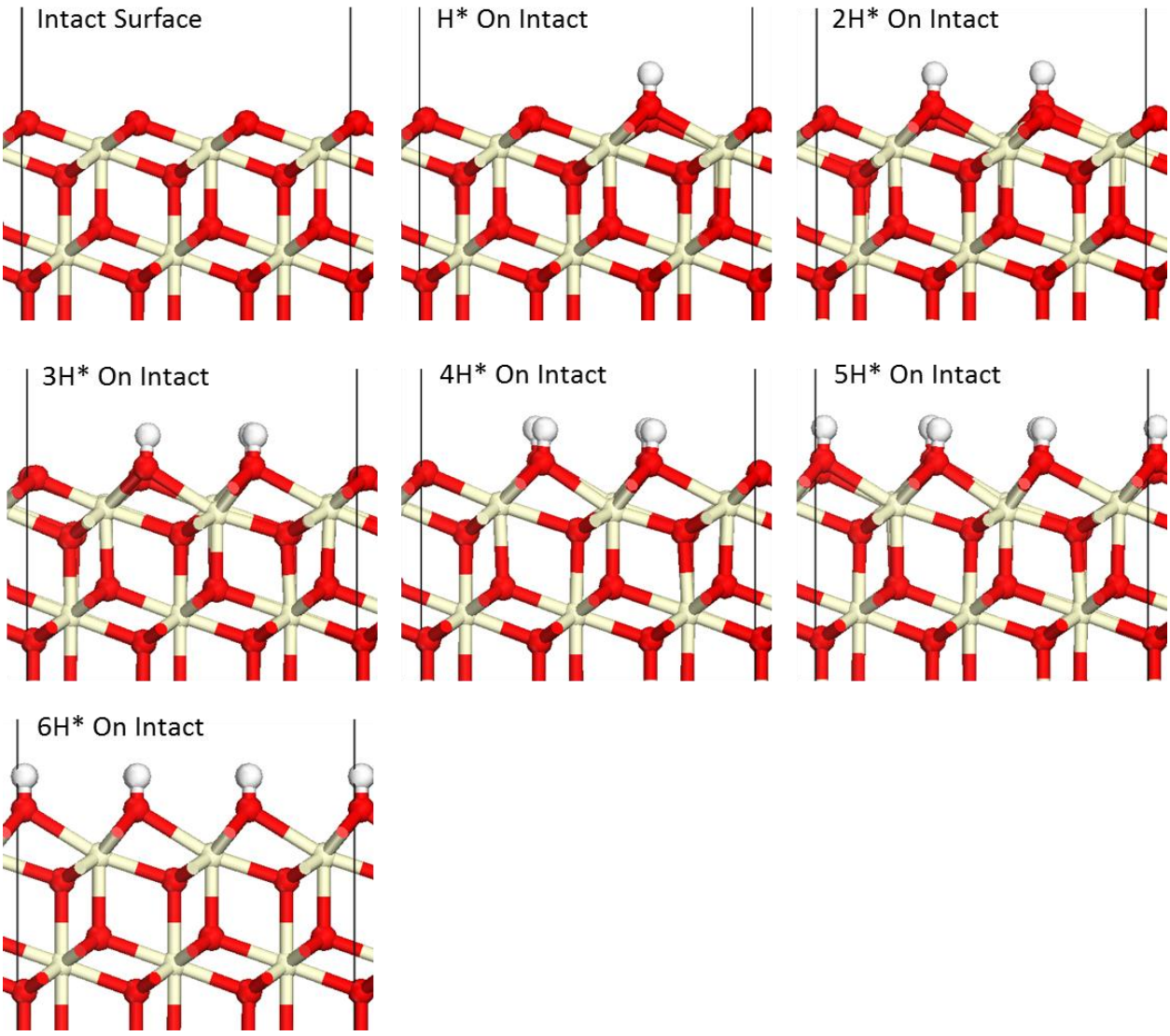

Figure S12. Structures for hydrogen adsorption on an intact CeO_2 surface. Ce is displayed as tan (light), O as red (dark).

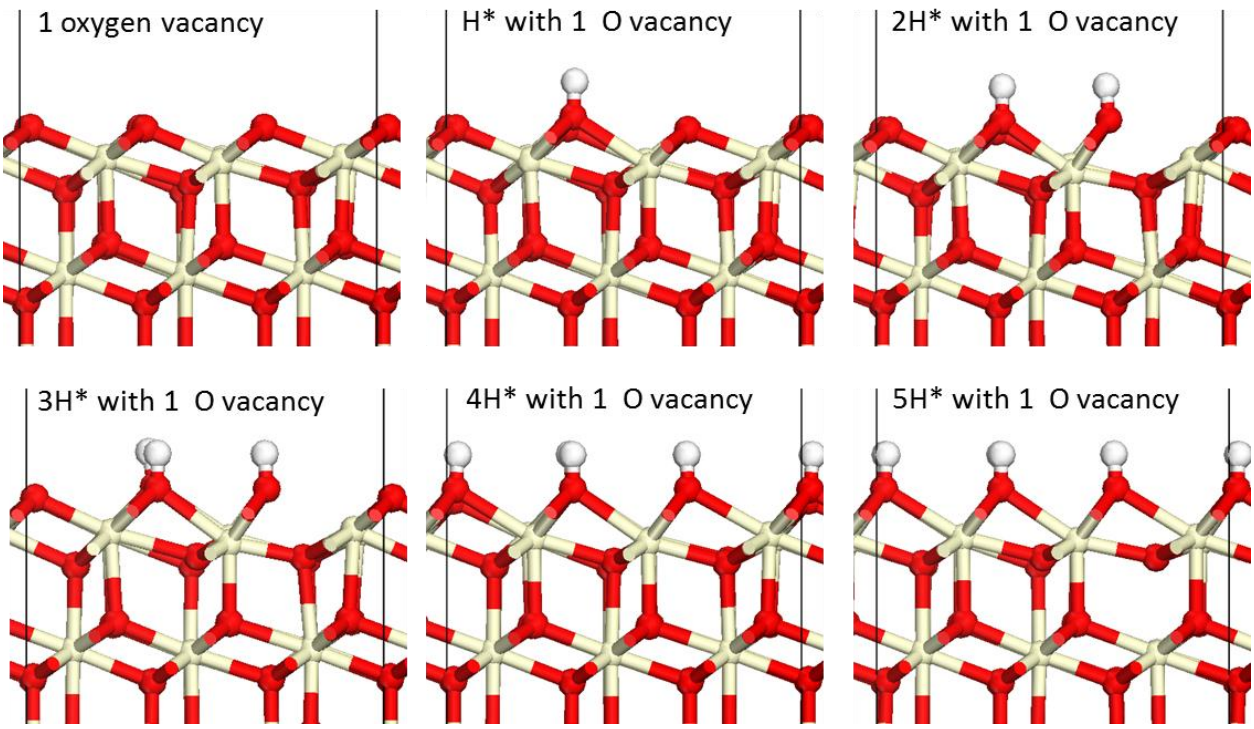

Figure S13. Structures for hydrogen adsorption on a CeO_2 surface with 1 oxygen vacancy. Ce is displayed as tan (light), O as red (dark).

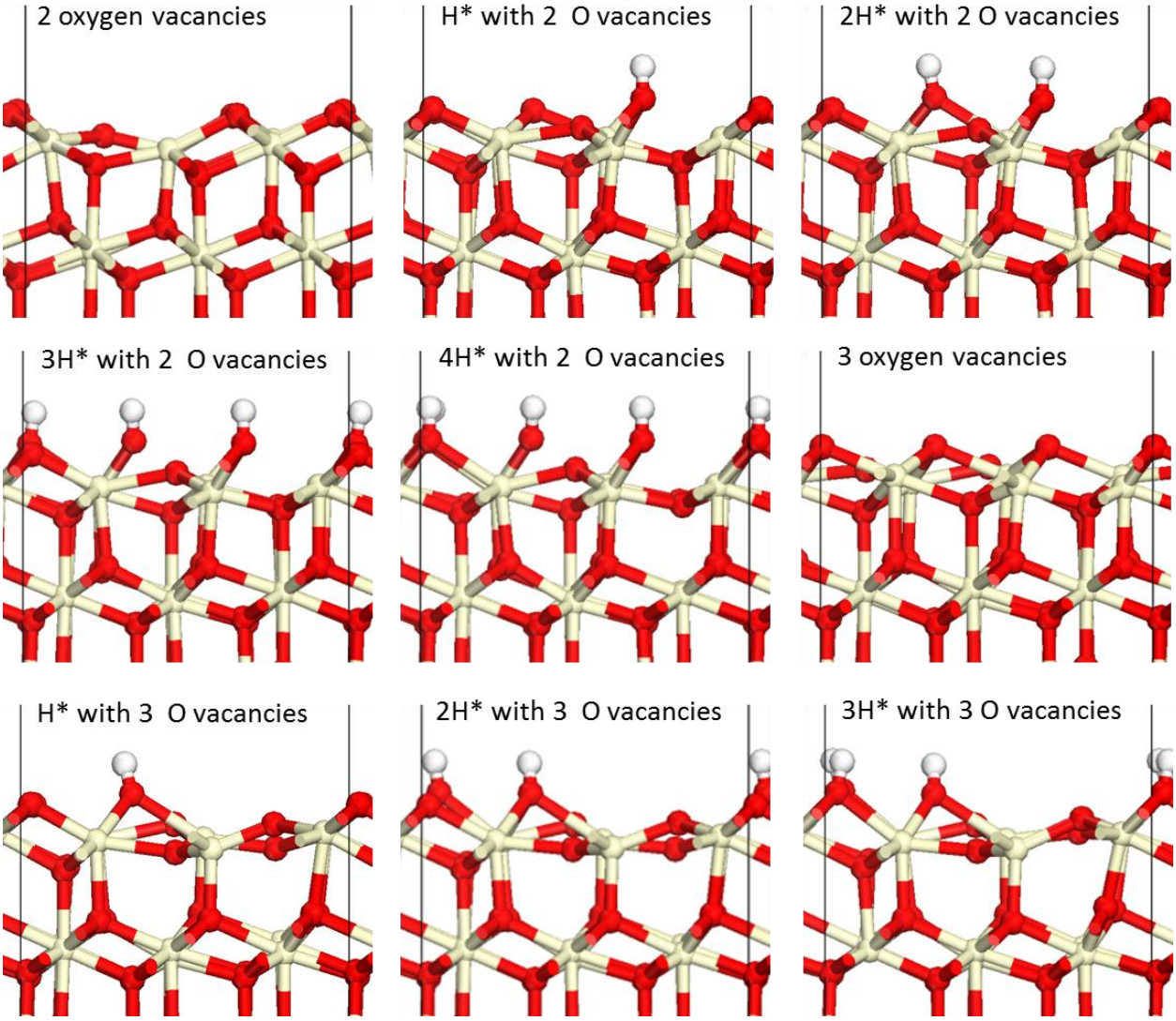

Figure S14 Structures for hydrogen adsorption on a CeO_2 surface with 2 and 3 oxygen vacancy. Ce is displayed as tan (light), O as red (dark).

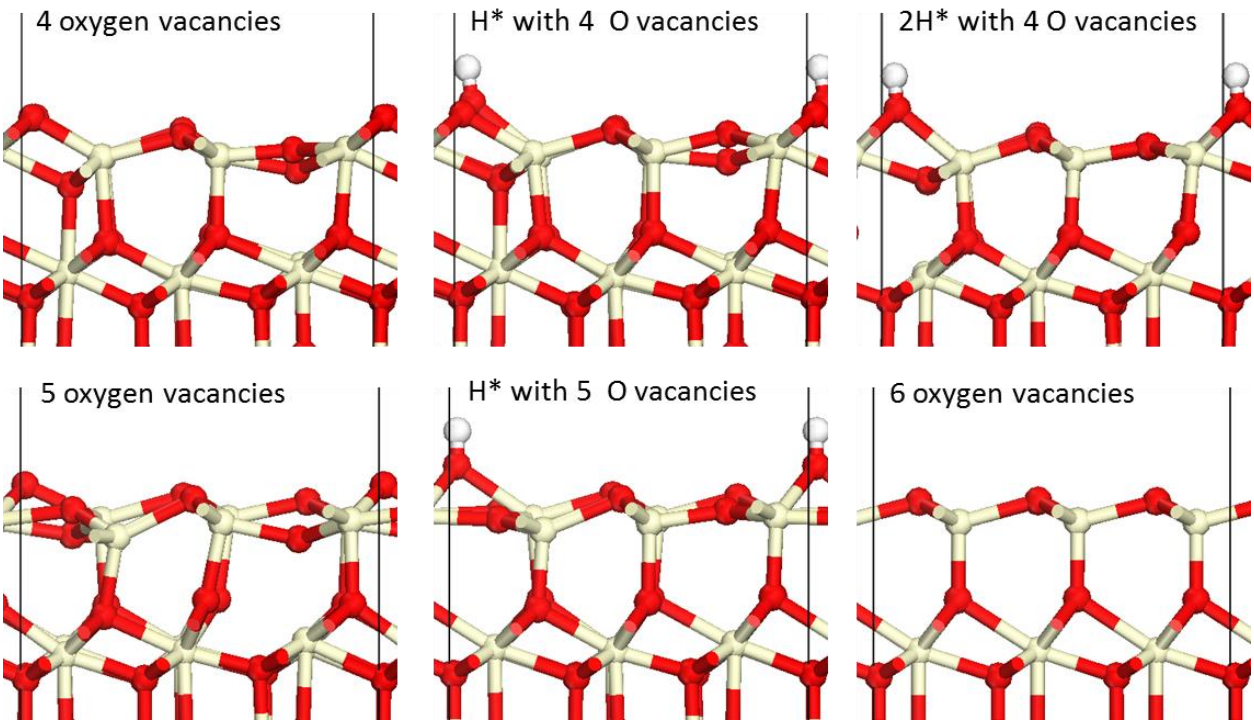

Figure S15. Structures for hydrogen adsorption on a CeO_2 surface with 4, 5 and 6 oxygen vacancy. Ce is displayed as tan (light), O as red (dark).