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

Supporting information for: Dehydrogenation of Methanol to Formaldehyde Catalyzed by Pristine and Defective Ceria Surfaces

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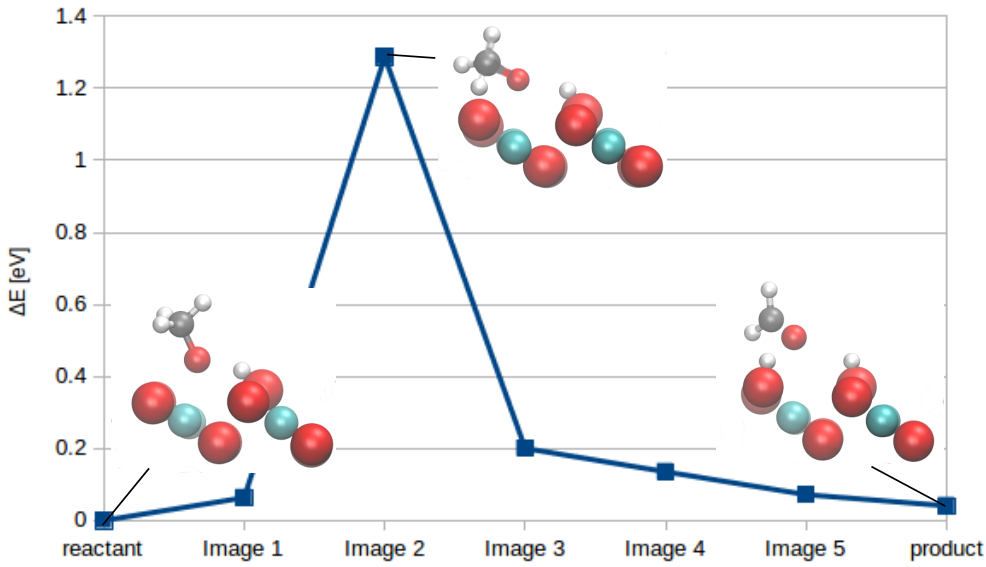

Figure S1: Methoxy to formaldehyde on the pristine (111) surface, energy difference in eV as a function of the reaction coordinate.

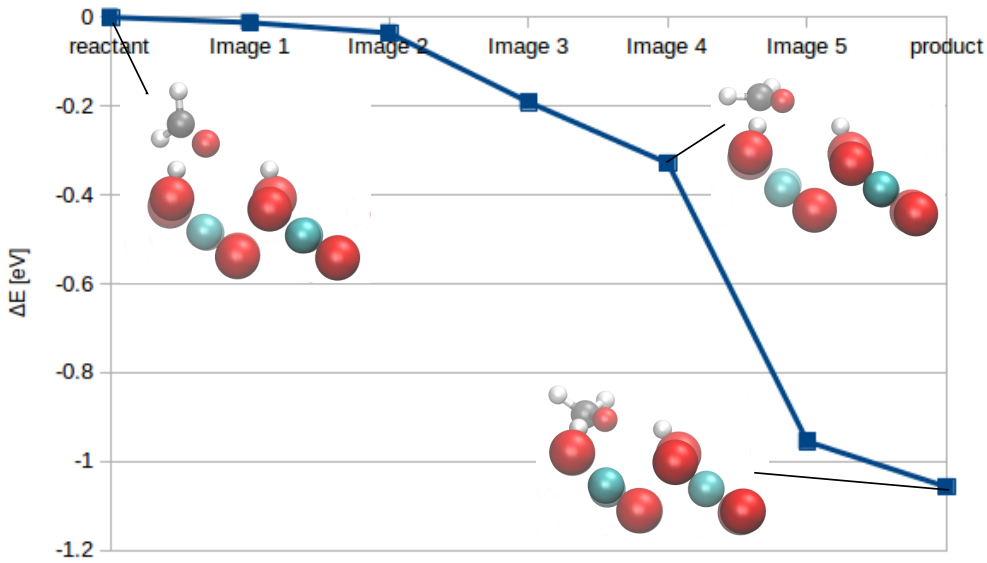

Figure S2: Formaldehyde to dioxymethylene on the pristine (111) surface, energy difference in eV as a function of the reaction coordinate.

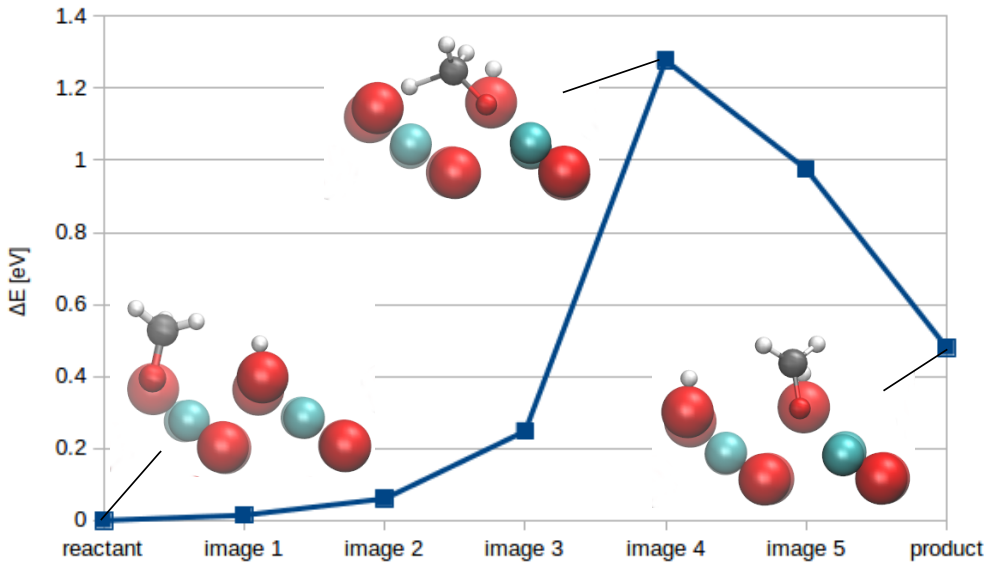

Figure S3: Methoxy to formaldehyde over a vacancy on the (111) surface, energy difference in eV as a function of the reaction coordinate.

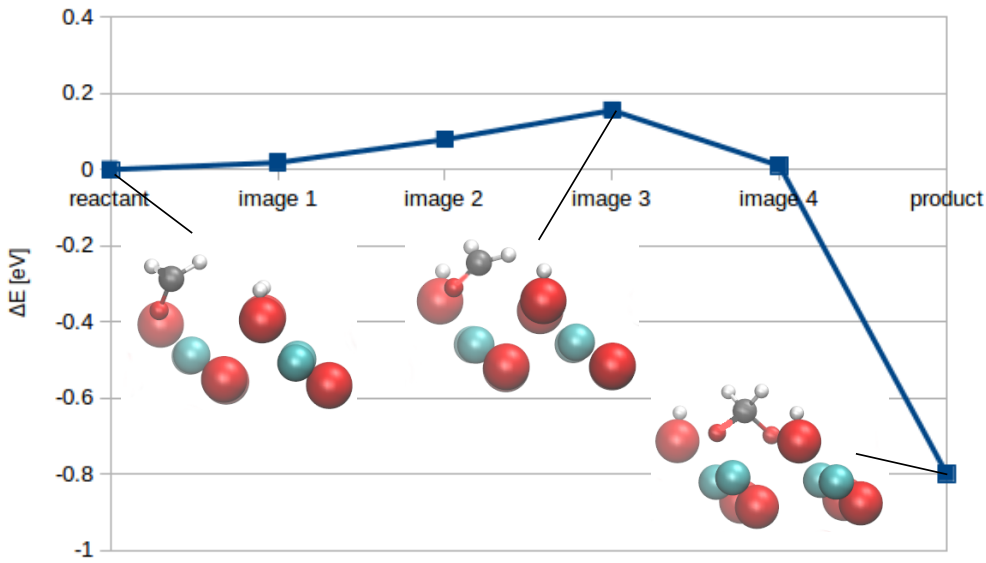

Figure S4: Formaldehyde to dioxymethylene over a vacancy on the (111) surface, energy difference in eV as a function of the reaction coordinate.

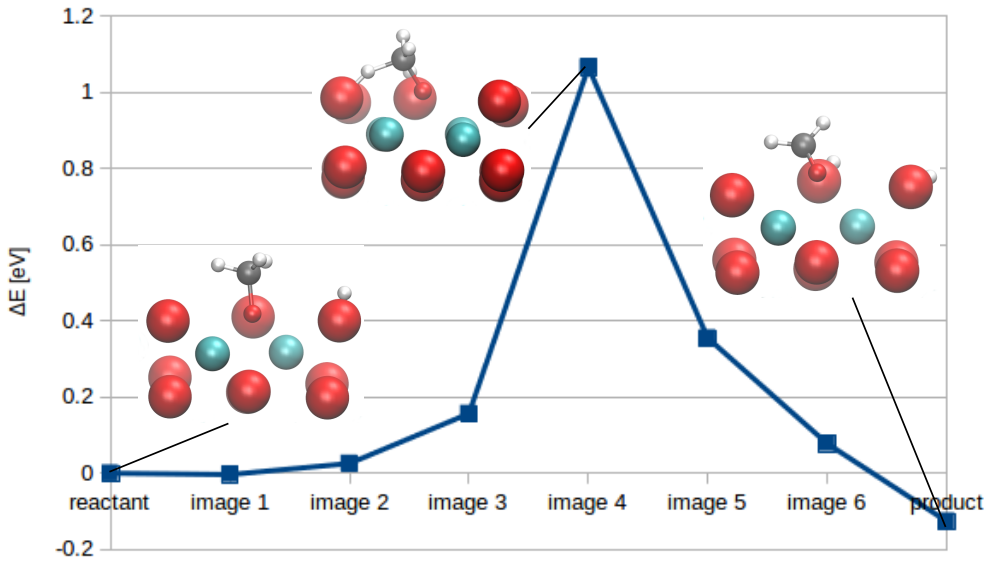

Figure S5: Methoxy to formaldehyde on the pristine (100) surface, surface hydrogen adjacent to each other, energy difference in eV as a function of the reaction coordinate.

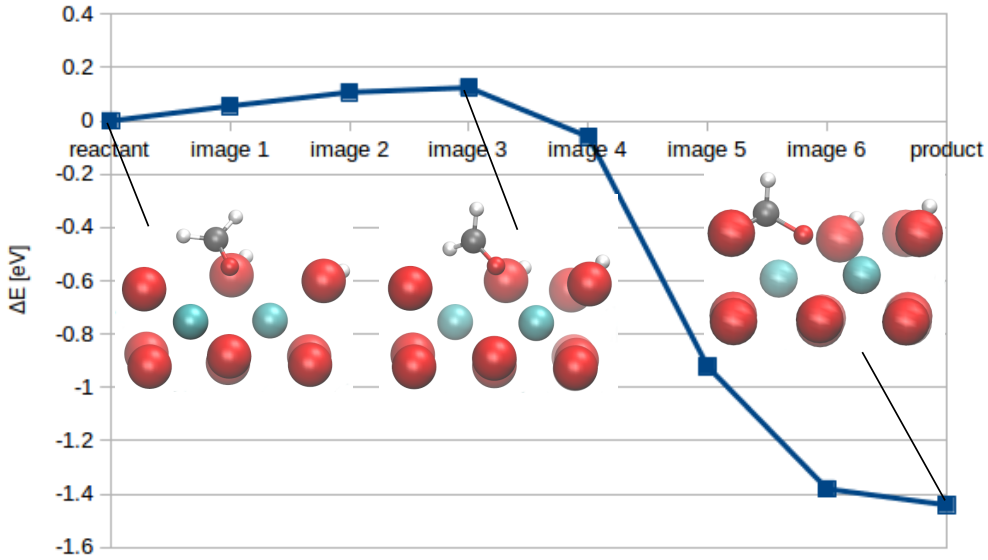

Figure S6: Formaldehyde to dioxymethylene on the pristine (100) surface, surface hydrogen adjacent to each other, energy difference in eV as a function of the reaction coordinate.

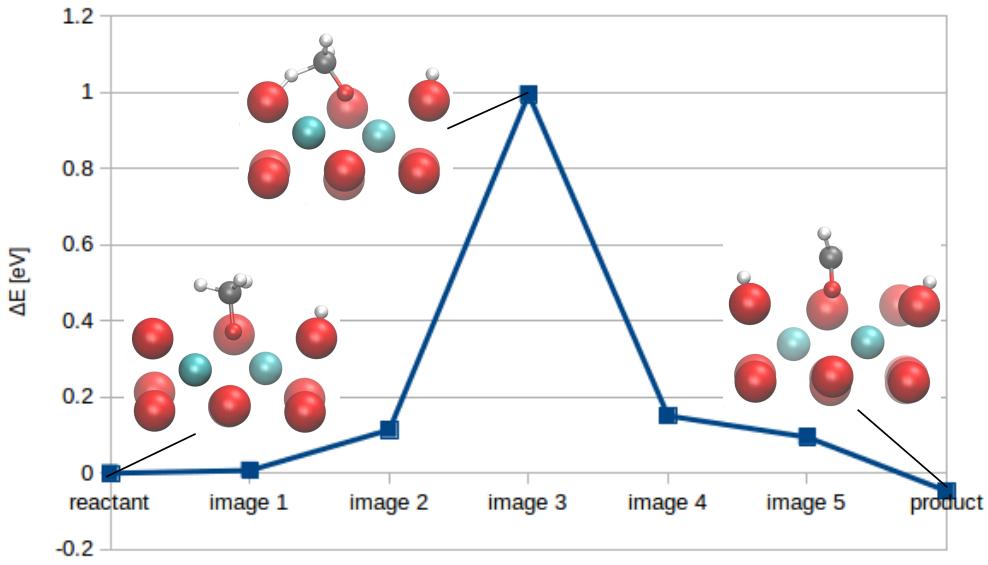

Figure S7: Methoxy to formaldehyde on the pristine (100) surface, surface hydrogen not adjacent to each other, energy difference in eV as a function of the reaction coordinate.

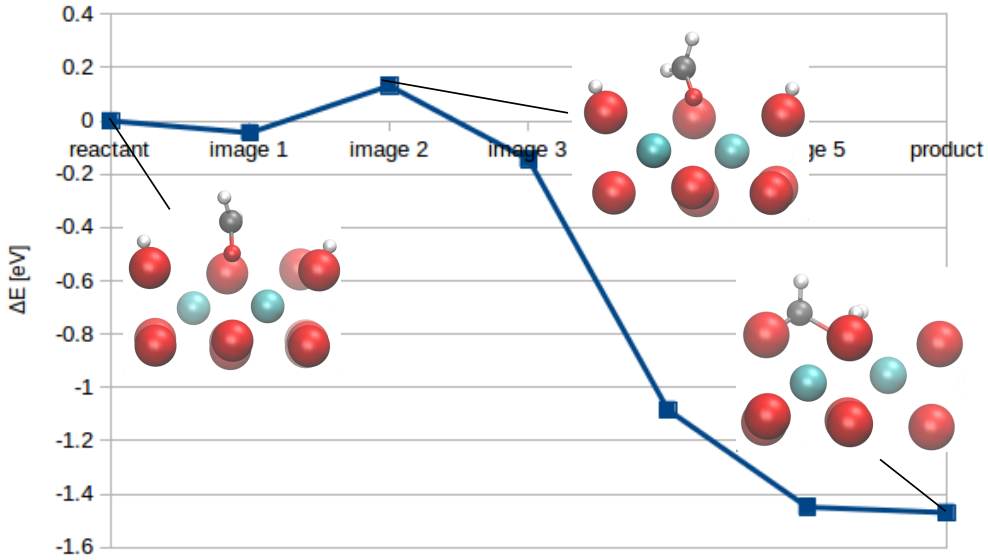

Figure S8: Formaldehyde to dioxymethylene on the pristine (100) surface, surface hydrogen not adjacent to each other, energy difference in eV as a function of the reaction coordinate.

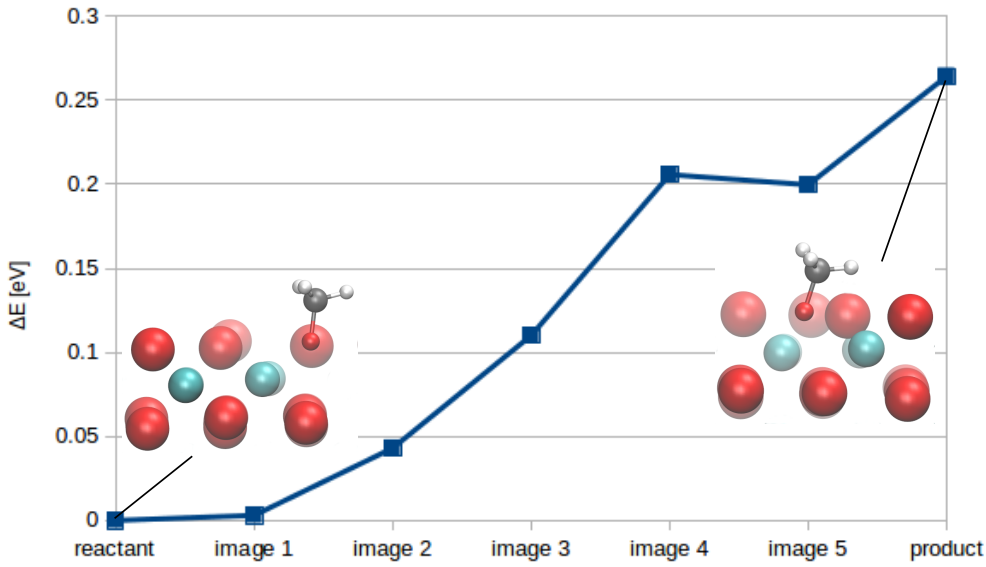

Figure S9: Methoxy migration from vacancy to next to vacancy position on the (100) surface, energy difference in eV as a function of the reaction coordinate.

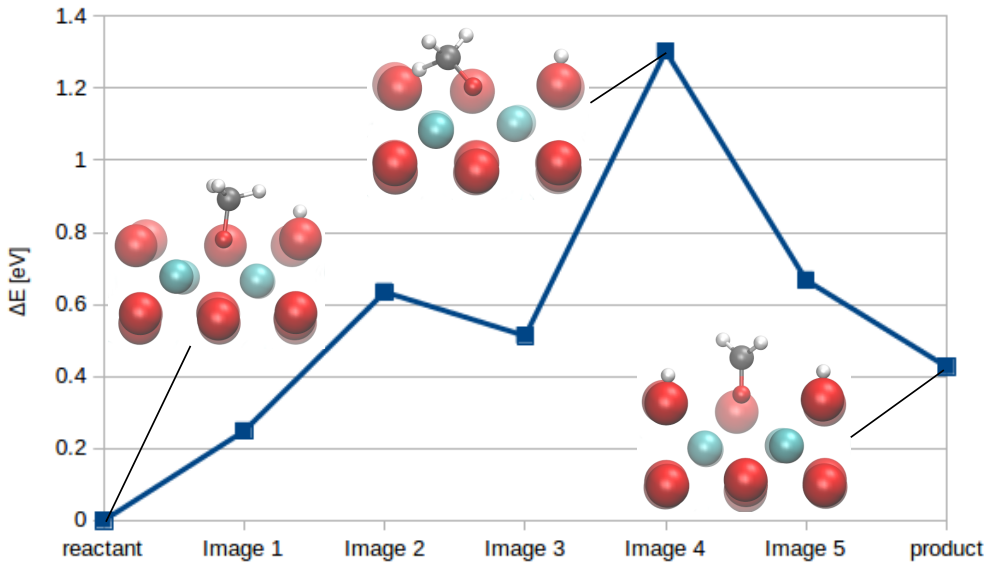

Figure S10: Methoxy to formaldehyde over a vacancy on the (100) surface, surface hydrogen not adjacent to each other, energy difference in eV as a function of the reaction coordinate.

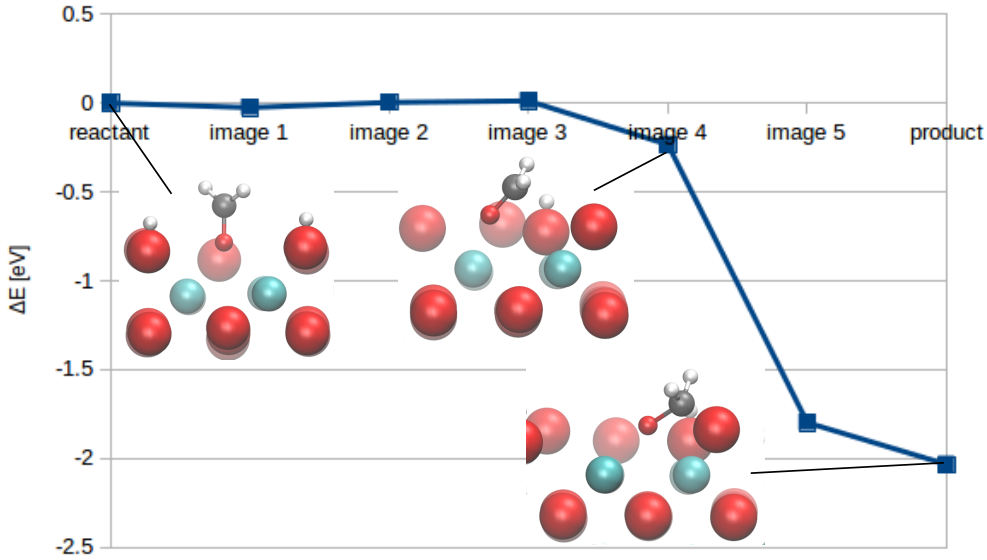

Figure S11: Formaldehyde to dioxymethylene over a vacancy on the (100) surface, surface hydrogen not adjacent to each other, energy difference in eV as a function of the reaction coordinate.

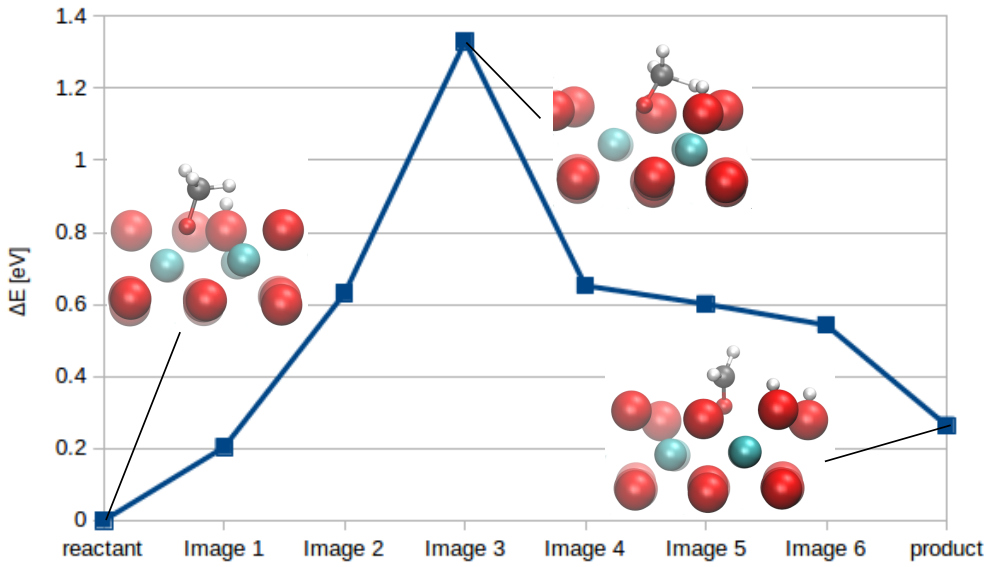

Figure S12: Methoxy to formaldehyde next to a vacancy on the (100) surface, surface hydrogen not adjacent to each other, energy difference in eV as a function of the reaction coordinate.

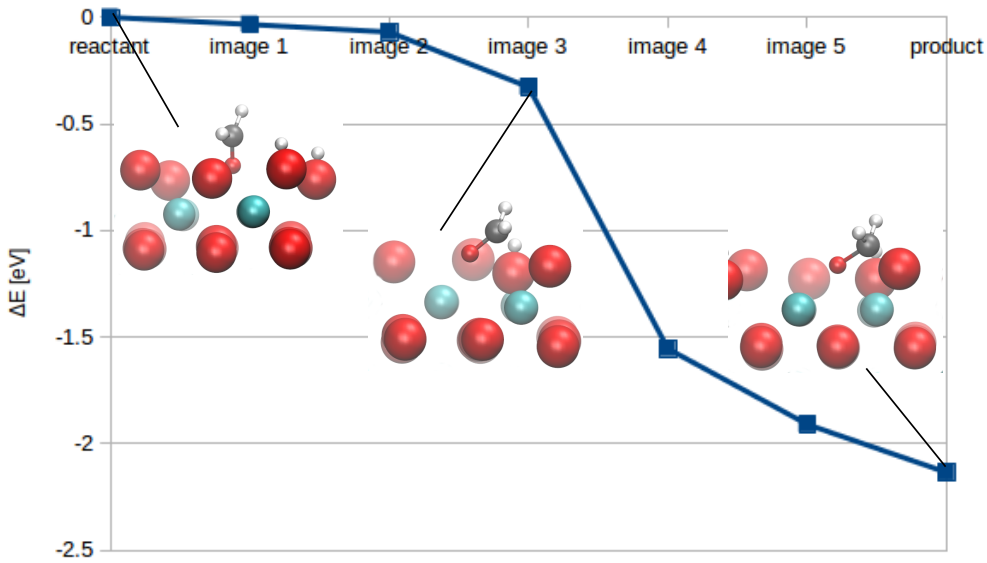

Figure S13: Formaldehyde to dioxymethylene next to a vacancy on the (100) surface, surface hydrogen not adjacent to each other, energy difference in eV as a function of the reaction coordinate.

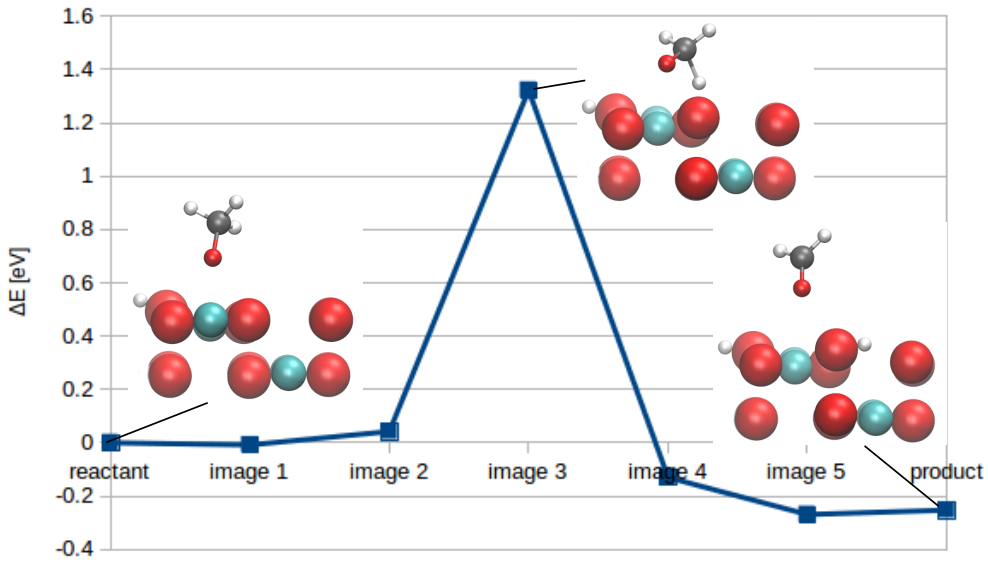

Figure S14: Methoxy to formaldehyde on the pristine (110) surface, surface hydrogen not adjacent to each other, energy difference in eV as a function of the reaction coordinate.

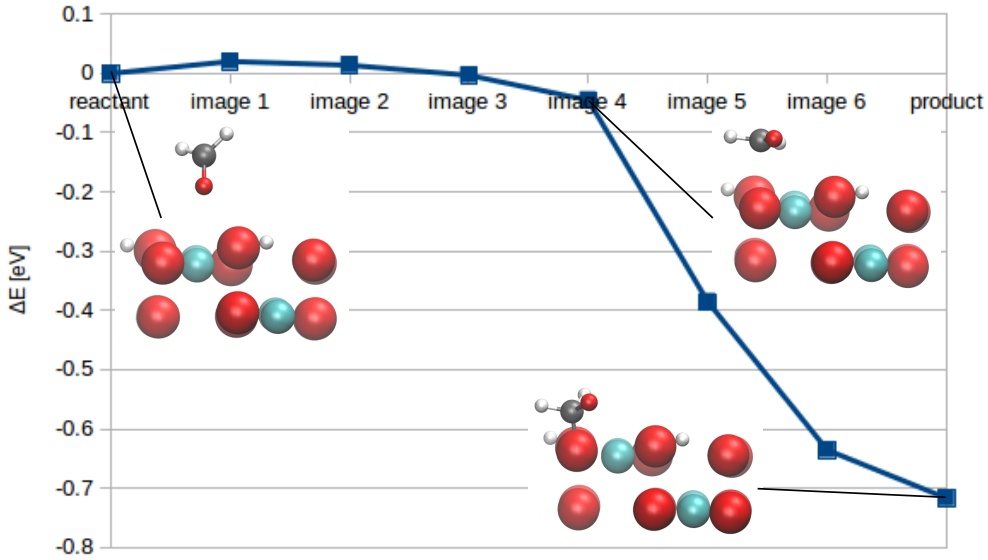

Figure S15: Formaldehyde to dioxymethylene on the pristine (110) surface, surface hydrogen not adjacent to each other, energy difference in eV as a function of the reaction coordinate.

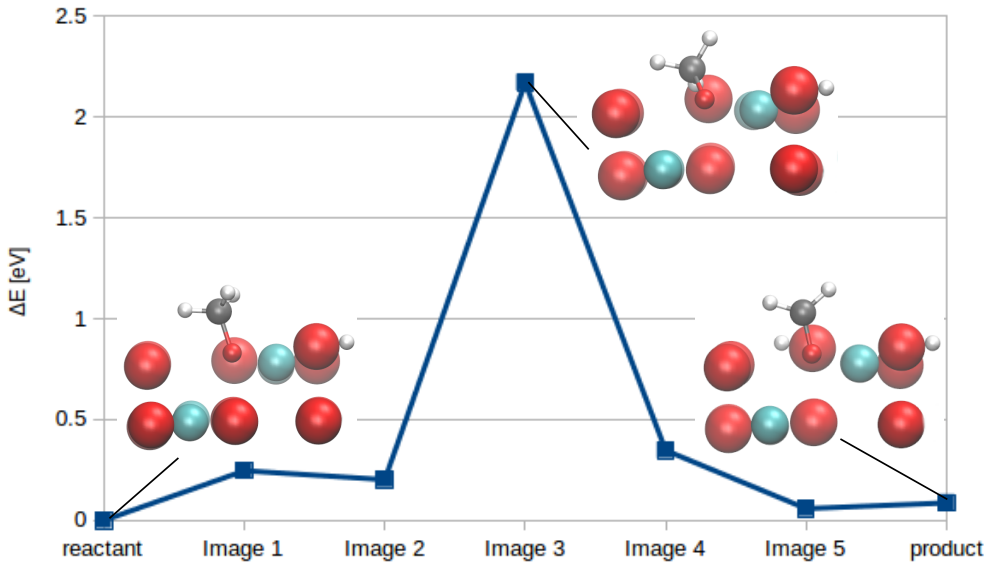

Figure S16: Methoxy to formaldehyde over a vacancy on the (110) surface, hydrogen transfer to neighbouring oxygen furthest from methoxy, energy difference in eV as a function of the reaction coordinate.

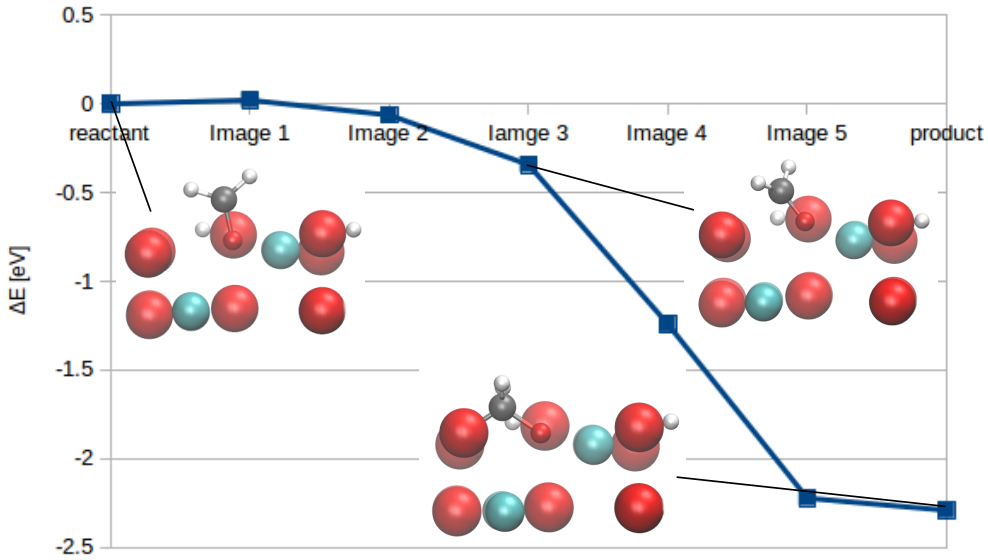

Figure S17: Formaldehyde to dioxymethylene over a vacancy on the (110) surface, hydrogen transfer to neighbouring oxygen furthest from methoxy, energy difference in eV as a function of the reaction coordinate.

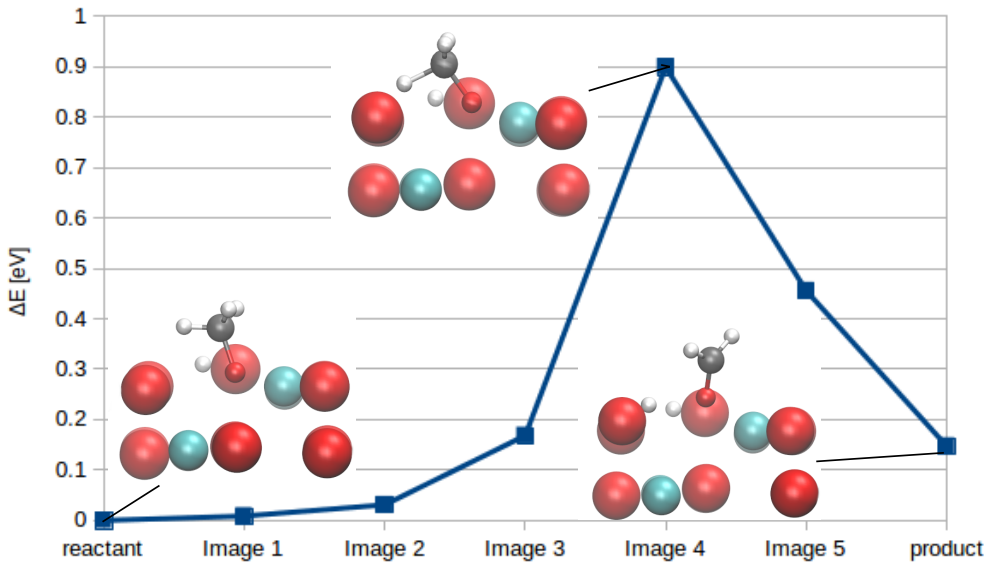

Figure S18: Methoxy to formaldehyde over a vacancy on the (110) surface, hydrogen transfer to neighbouring oxygen closest to methoxy and not hindered by cerium, energy difference in eV as a function of the reaction coordinate.

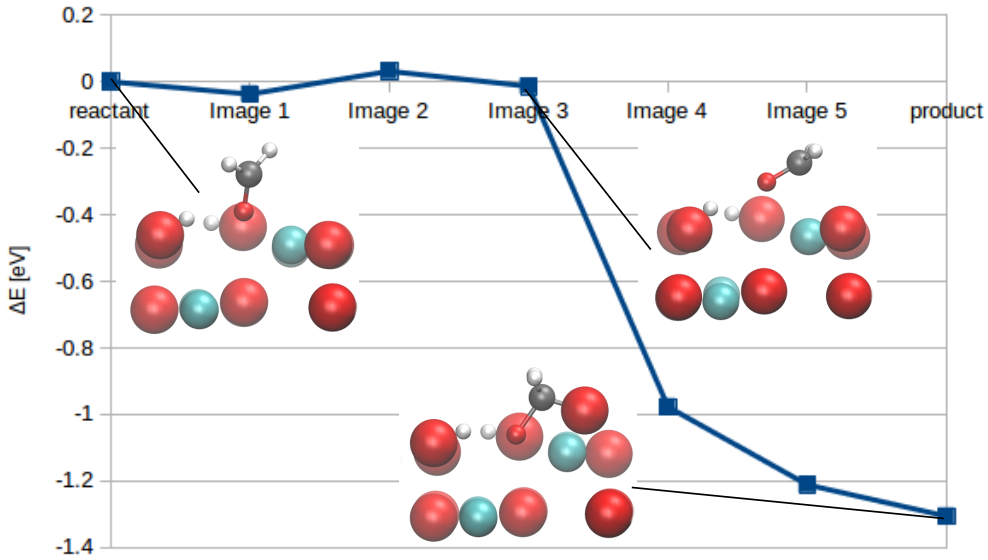

Figure S19: Formaldehyde to hydroxyoxymethylene over a vacancy on the (110) surface, hydrogen transfer to neighbouring oxygen closest to methoxy and not hindered by cerium, energy difference in eV as a function of the reaction coordinate.

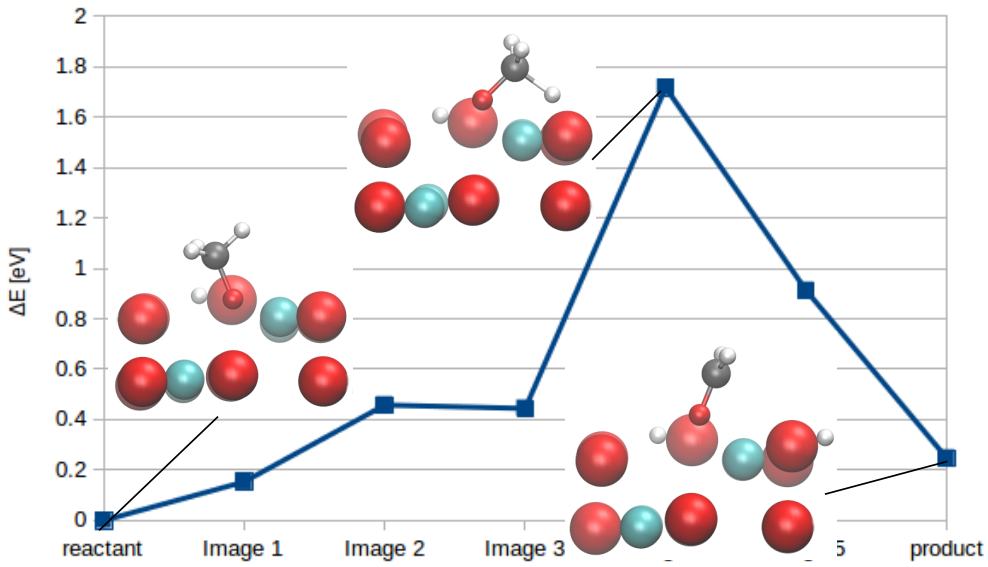

Figure S20: Methoxy to formaldehyde over a vacancy on the (110) surface, hydrogen transfer to neighbouring oxygen closest to methoxy and hindered by cerium, energy difference in eV as a function of the reaction coordinate.

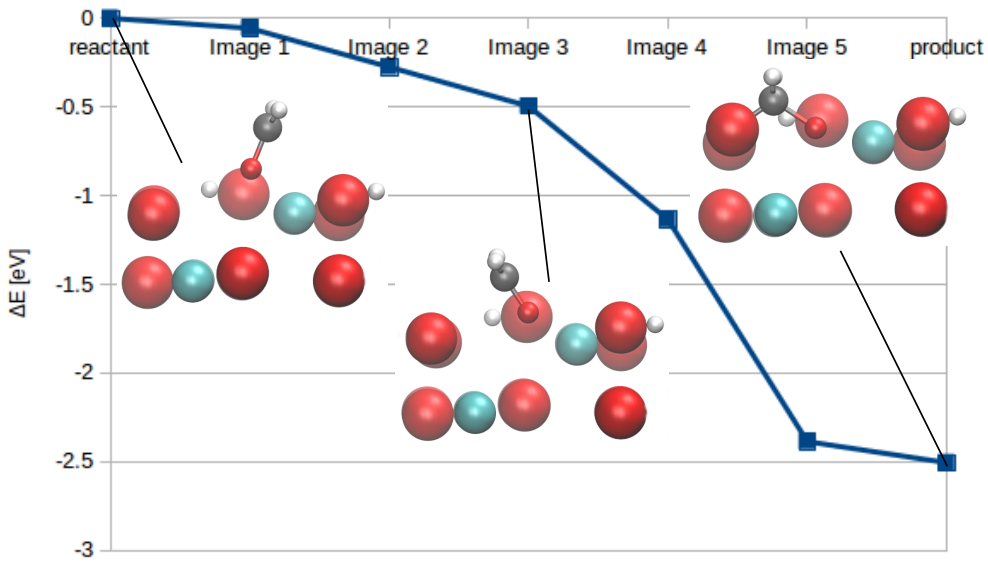

Figure S21: Formaldehyde to dioxymethylene over a vacancy on the (110) surface, hydrogen transfer to neighbouring oxygen closest to methoxy and hindered by cerium, energy difference in eV as a function of the reaction coordinate.

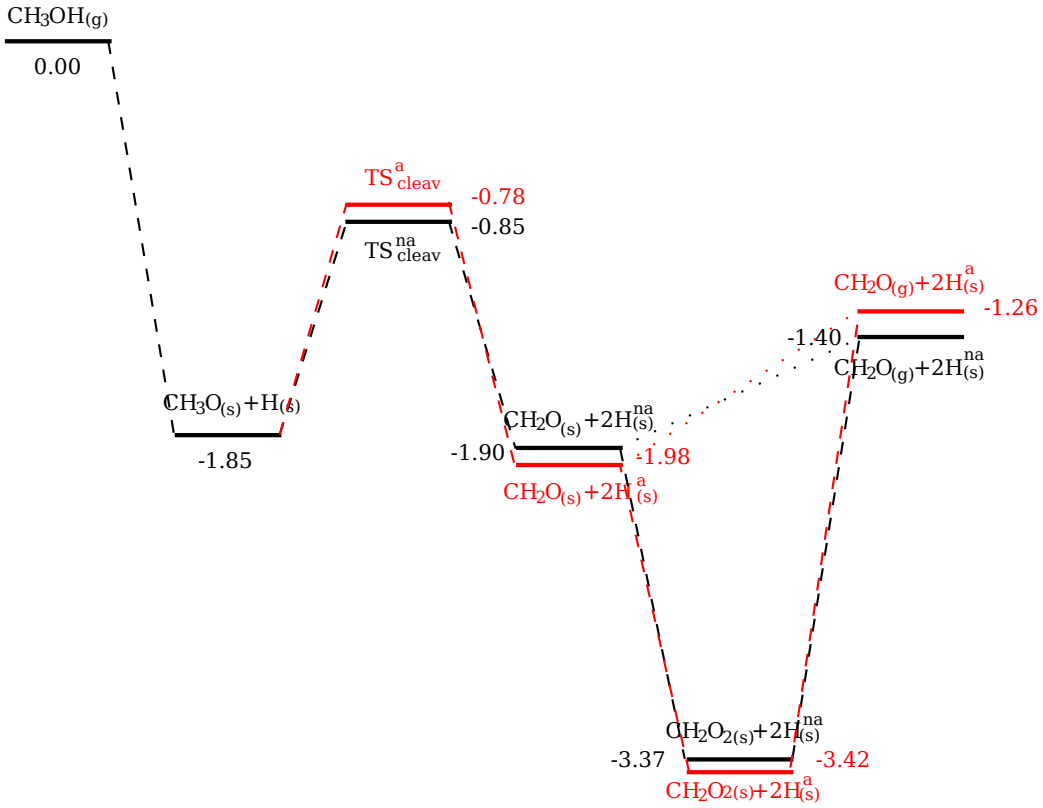

Figure S22: Energy profile for methanol conversion to formaldehyde on the (100) surface comparing the relative position of the coadsorbed hydrogen atoms whether adjacent (superscript a, red lines) or not adjacent (superscript na, black lines); energies in eV, subscript (g) indicates gas phase, subscript (s) denotes adsorbed on surface, TS_{cleav} is the transition state for methoxy C-H cleavage.

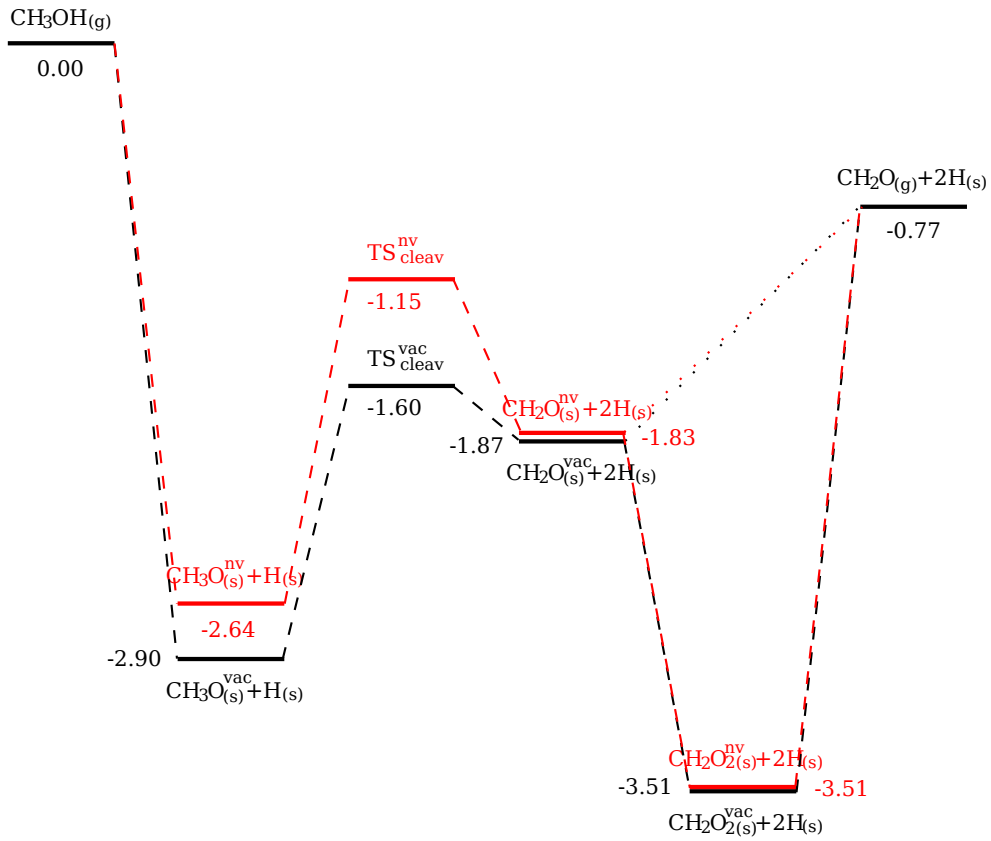

Figure S23: Energy profile for methanol conversion to formaldehyde on the defective (100) surface comparing conversion over a vacancy (superscript vac, black lines) and next to a vacancy (superscript nv, red lines); energies in eV, subscript (g) indicates gas phase, subscript (s) denotes adsorbed on surface, TS_{cleav} is the transition state for methoxy C-H cleavage.

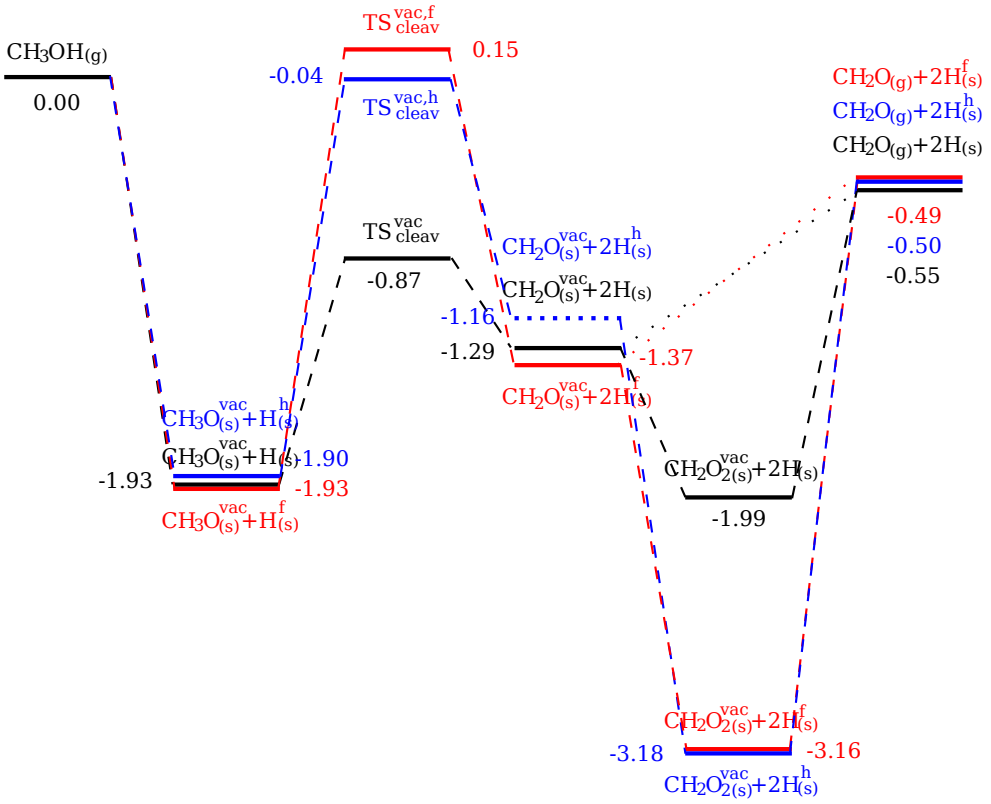

Figure S24: Energy profile for methanol conversion to formaldehyde on the defective (110) surface comparing hydrogen transfer to different neighbouring surface oxygen atoms: furthest from methoxy location (superscript vac,f; red lines), closest to methoxy (superscript vac, red lines), and closest to methoxy but hindered by surface cerium atoms (superscript vac,h; blue lines); energies in eV, subscript (g) indicates gas phase, subscript (s) denotes adsorbed on surface, TS_{cleav} is the transition state for methoxy C-H cleavage; dotted blue line for monodentate formaldehyde indicates that optimization did not converge and species was only identified along NEB path.

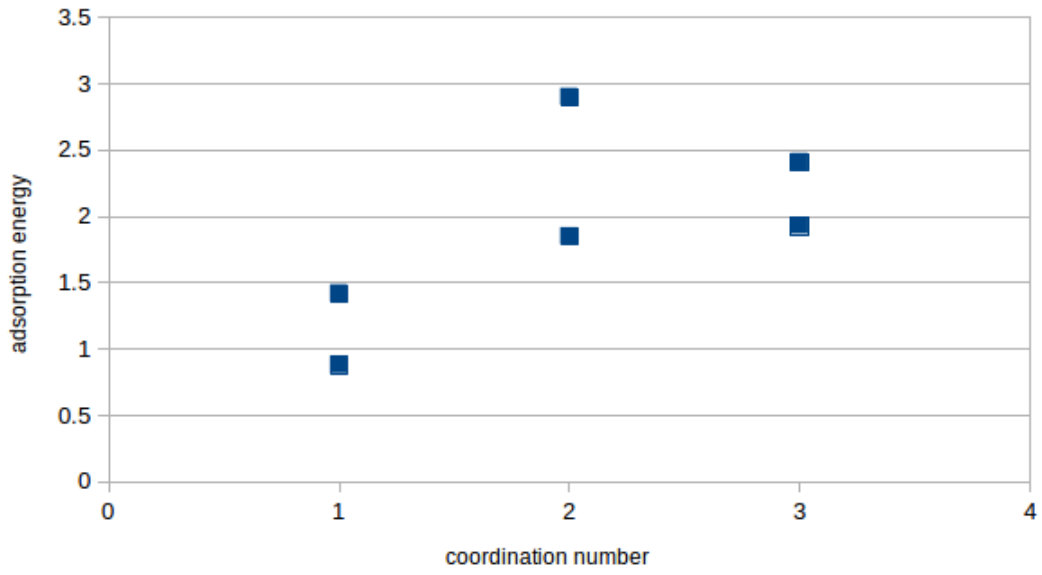

Figure S25: Dissociative adsorption energies of methanol as a function of Ce-methoxy coordination number.

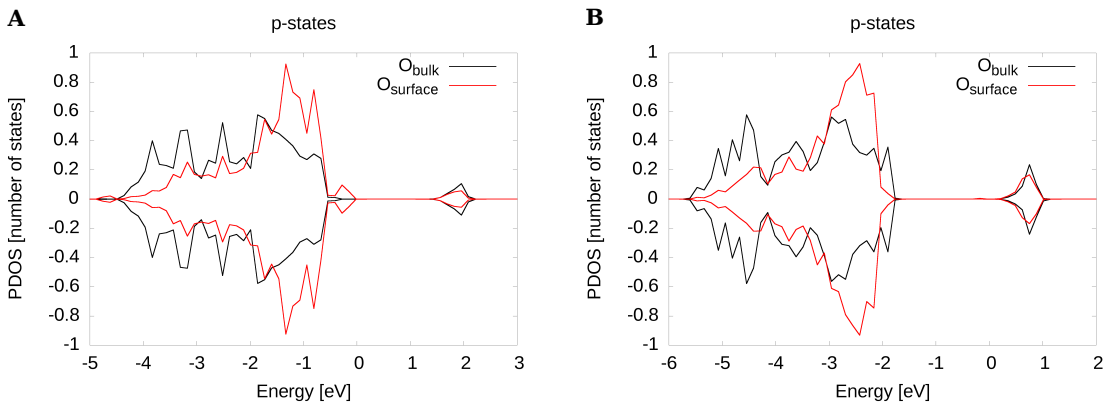

Figure S26: Projected density of state as a function of energy per unit cell and atom for the highest occupied p-band of surface oxygen (surf) to which hydrogen is transferred and a 4th layer oxygen (bulk) compared for methoxy on the (111) surface for A - pristine surface, B - over a vacancy.

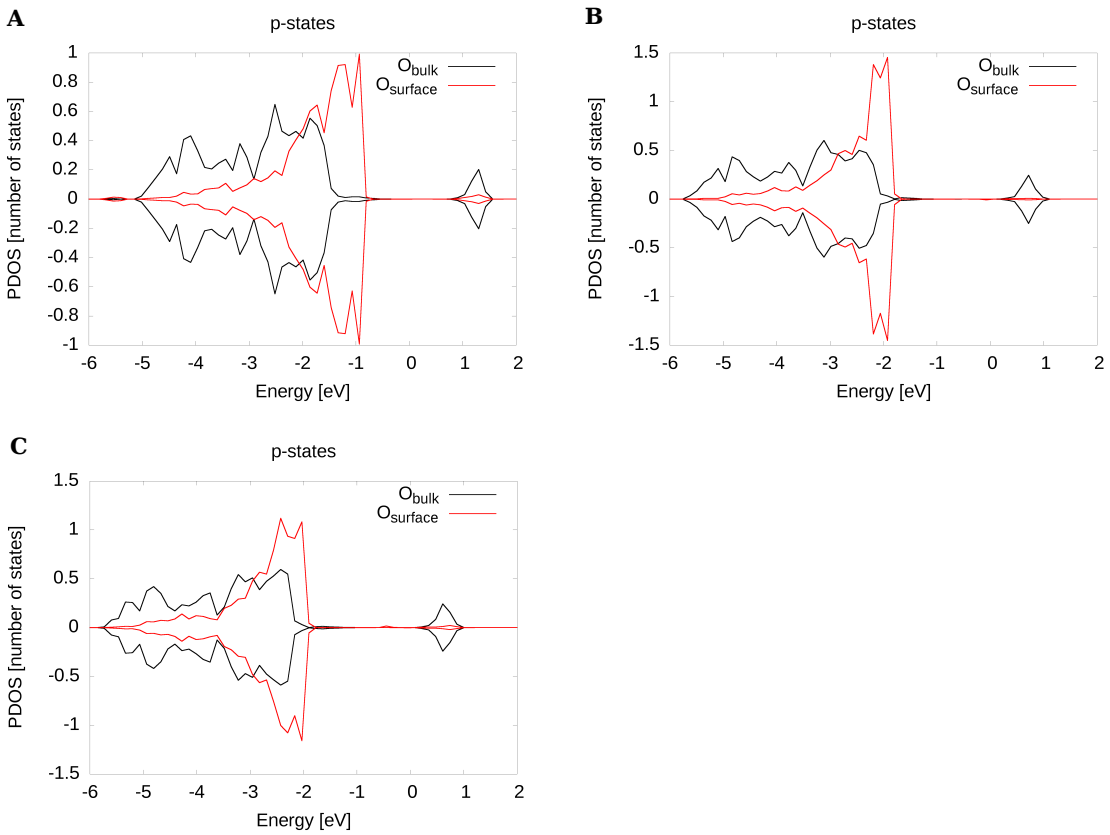

Figure S27: Projected density of state as a function of energy per unit cell and atom for the highest occupied p-band of surface oxygen (surf) to which hydrogen is transferred and a 4th layer oxygen (bulk) compared for methoxy on the (100) surface for A - pristine surface, B - over a vacancy, C - next to vacancy.

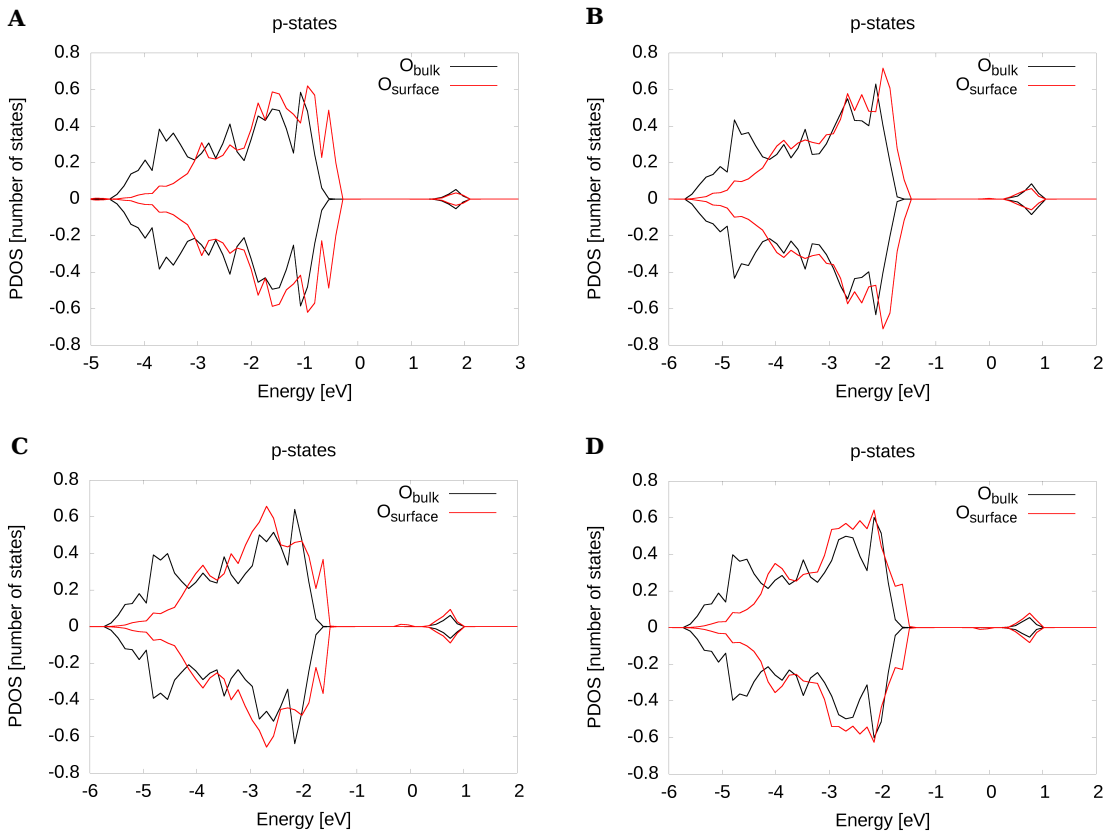

Figure S28: Projected density of state as a function of energy per unit cell and atom for the highest occupied p-band of surface oxygen (surf) to which hydrogen is transferred and a 4th layer oxygen (bulk) compared for methoxy on the (110) surface for A - pristine surface, B - over a vacancy, neighbouring O closest to methoxy, C - over a vacancy, neighbouring O closest to methoxy, hindered by Ce, D - over a vacancy, neighbouring O furthest from methoxy.