catalysts

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Article

Investigations of the effect of H_2 in CO oxidation over ceria catalysts

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Received: 9 December 2021; Accepted: 11 December 2021; Published: 20 December 2021

X-ray diffraction

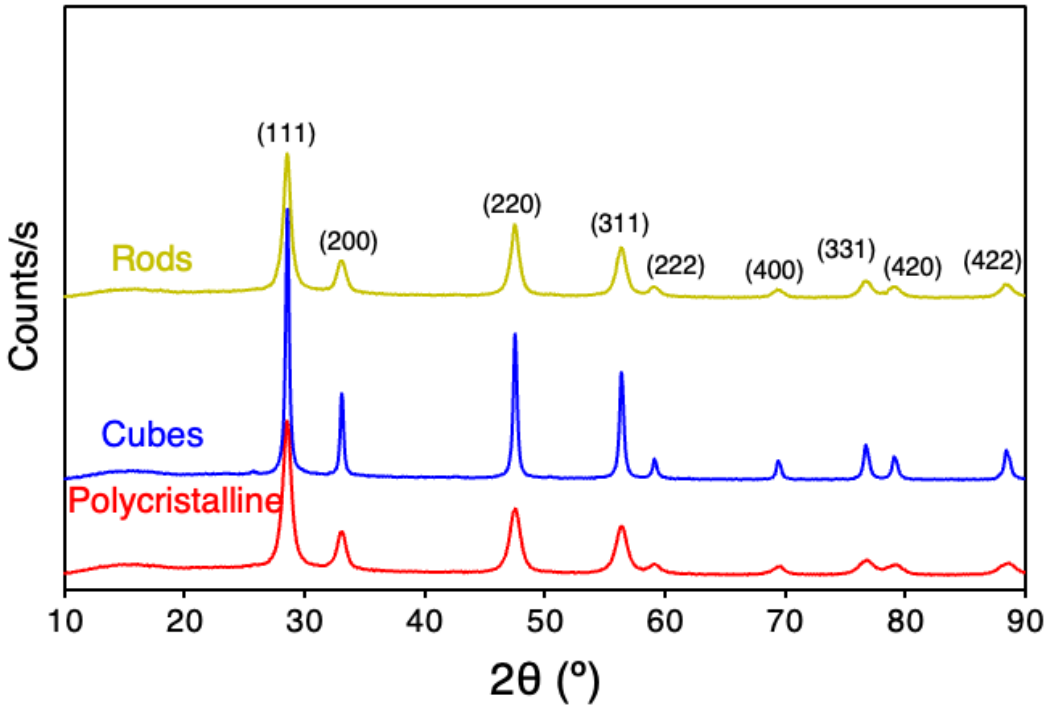

Figure S1. X-ray diffractograms of polycrystalline ceria, nano cubes and nano rods. All diffractograms display CeO_2 crystalline features (JCPDS 34–0394).

X-ray photoelectronic spectroscopy

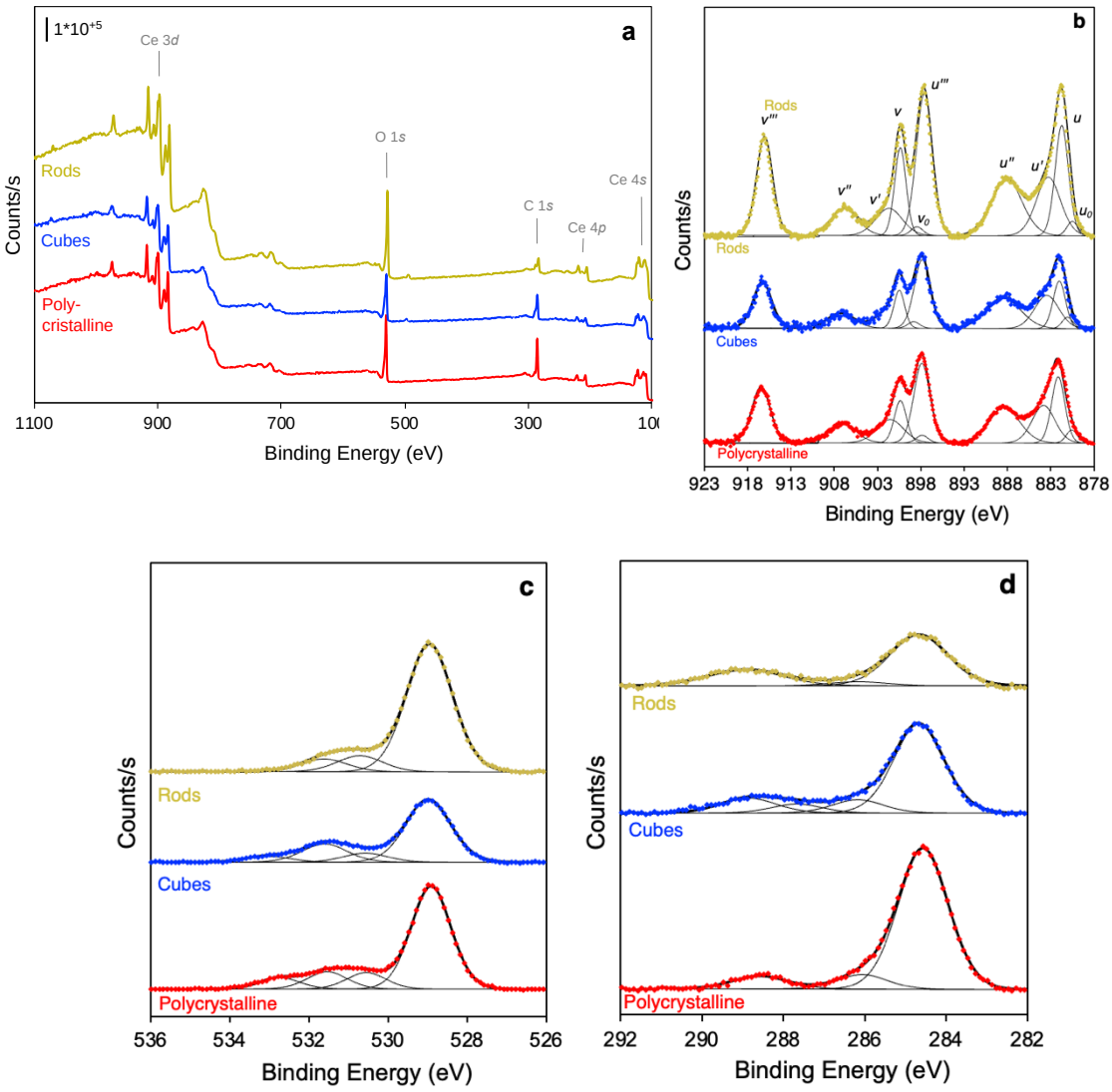

Figure S2. XPS characterization: (a) survey spectra; (b) Ce 3d; (c) O 1s and (d) C 1s XPS regions.

Transmission electron microscopy

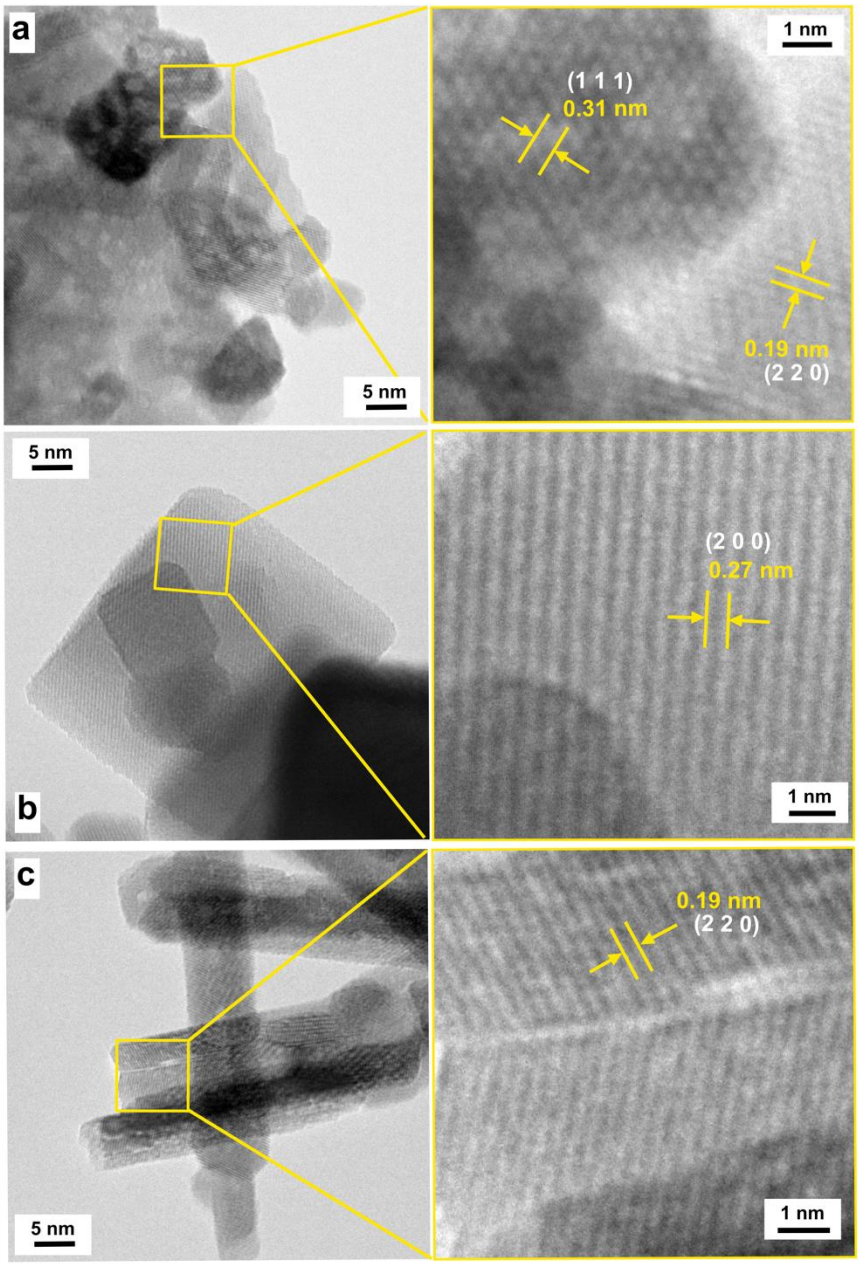

Figure S3. TEM images of: (a) polycrystalline ceria; (b) nanocubes; (c) nanorods exhibiting characteristic lattice interplanar fringes.

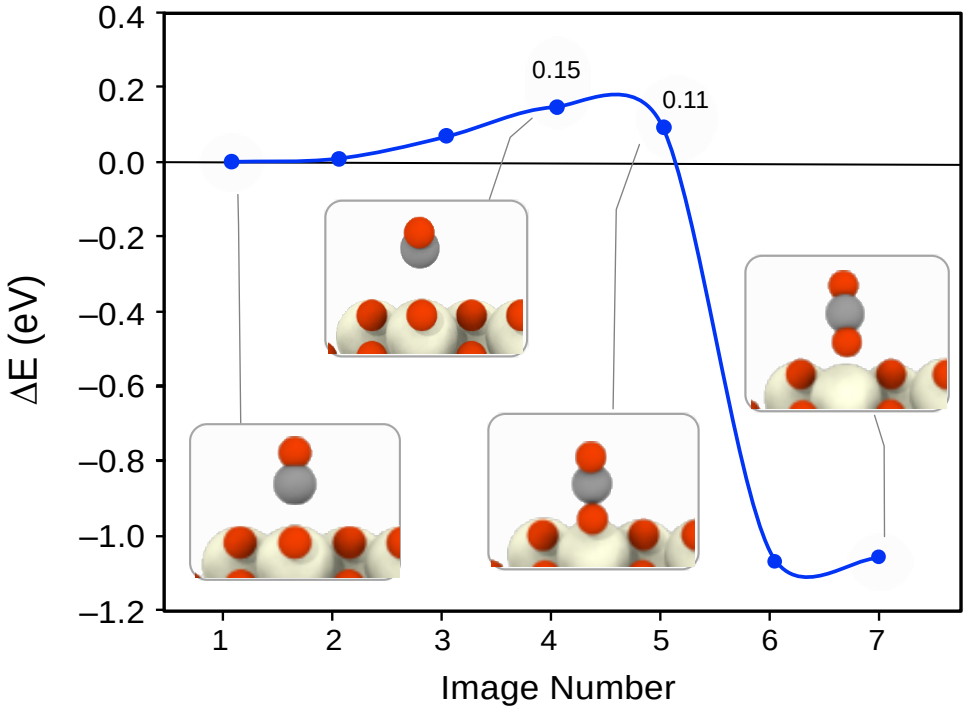

Figure S4. CI-NEB calculation of CO oxidation on a clean ceria(111) surface: CO(gas) + O^{2-}(lat) → CO_2^{2-}(ads)

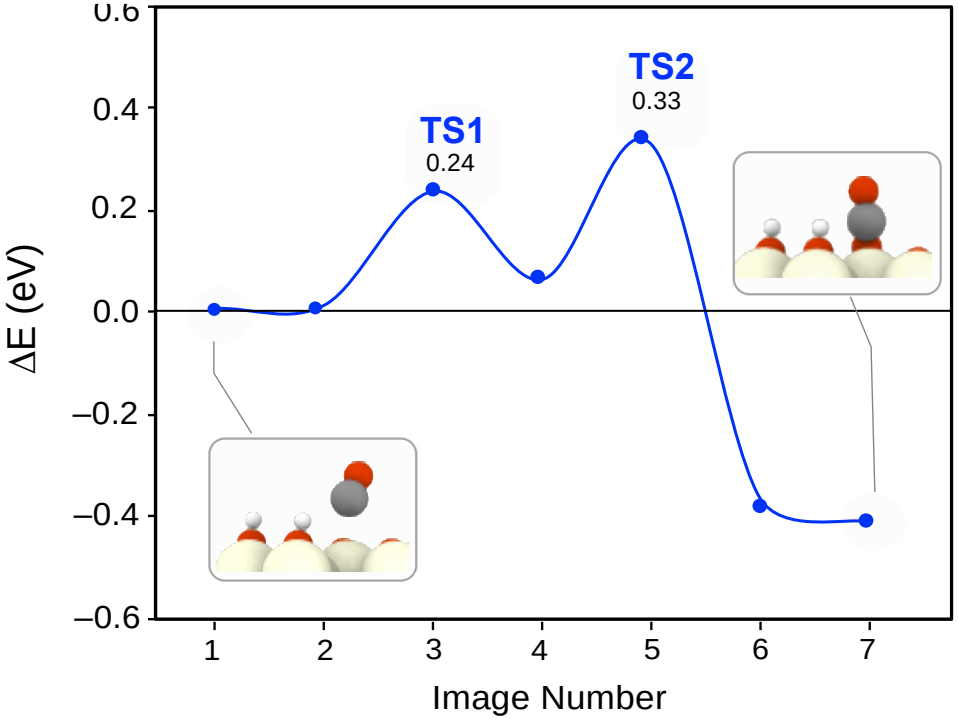

Figure S5. CI-NEB calculation of the formation of carboxylate on a 2 OH-covered ceria(111) surface: CO(gas) + O^{2-}(lat) → CO_2^{2-}(ads)

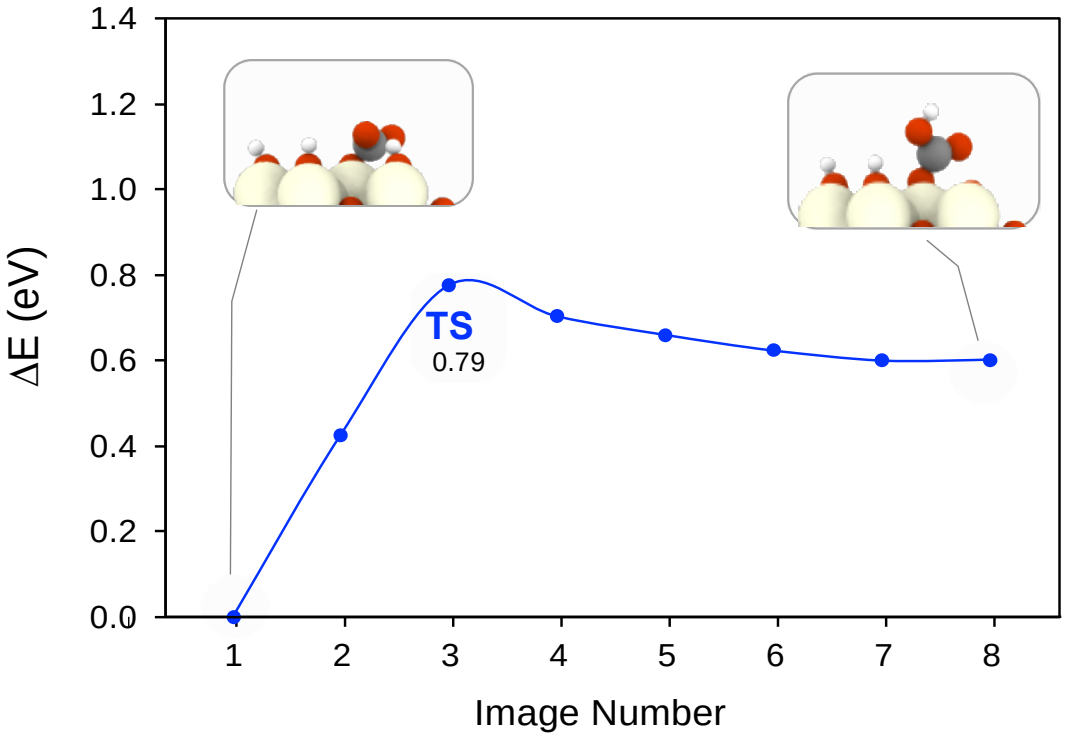

Figure S6. CI-NEB calculation of the bicarbonate formation upon proton transfer to carbonate on a 3 OH-covered ceria(111) surface.

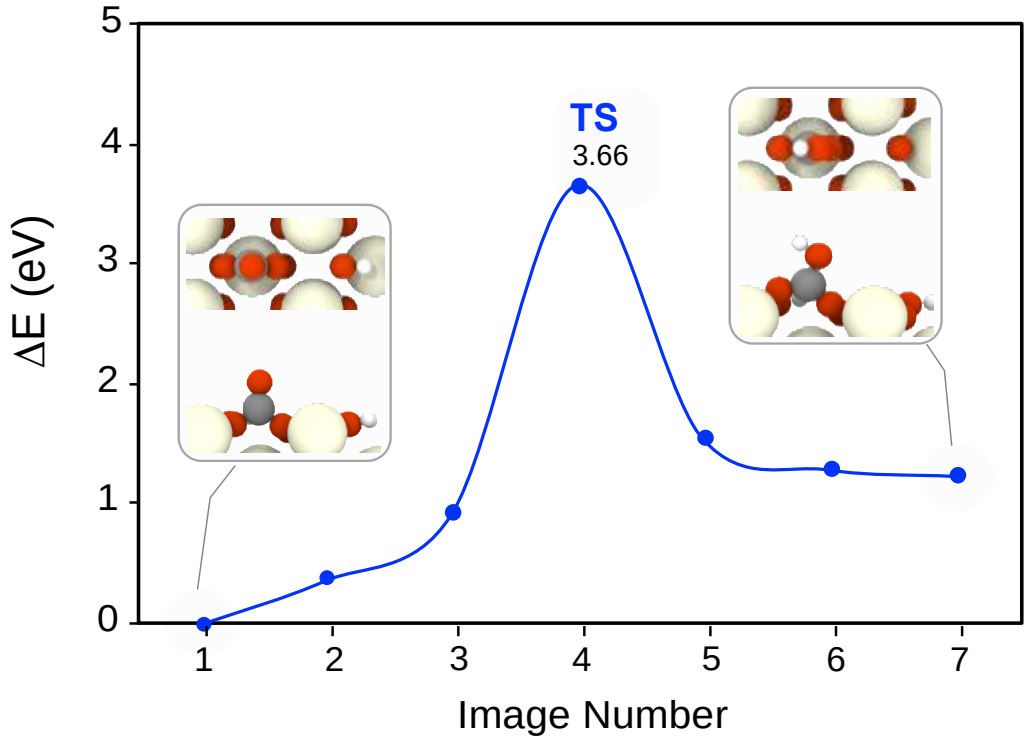

Figure S7. CI-NEB calculation of the bicarbonate Type A formation upon proton transfer to carbonate on a 3 OH-covered ceria(110) surface.

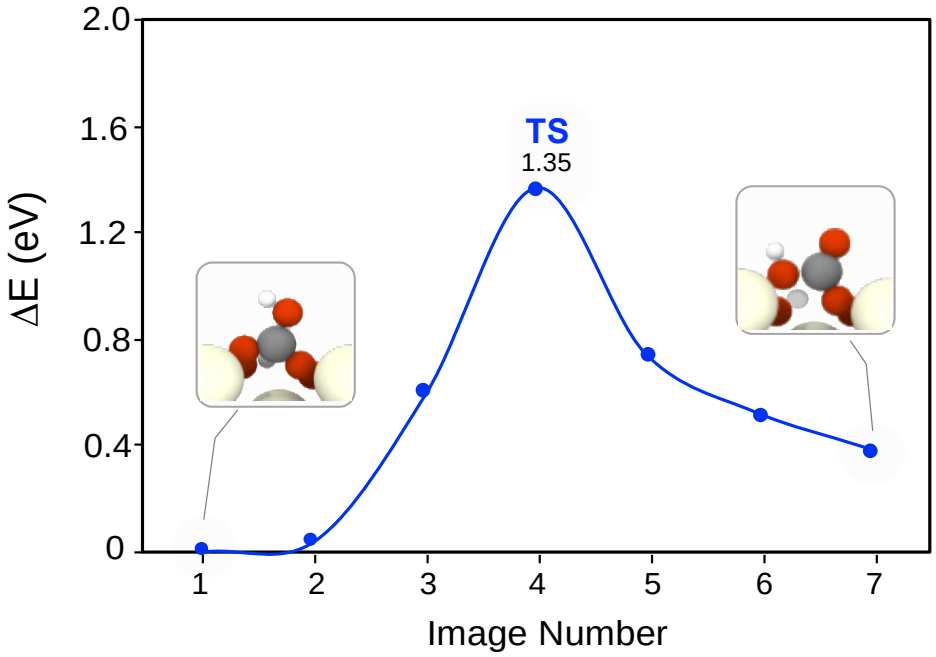

Figure S8. CI-NEB calculation of the bicarbonate Type A transformation to bicarbonate Type B on the ceria(110) surface.

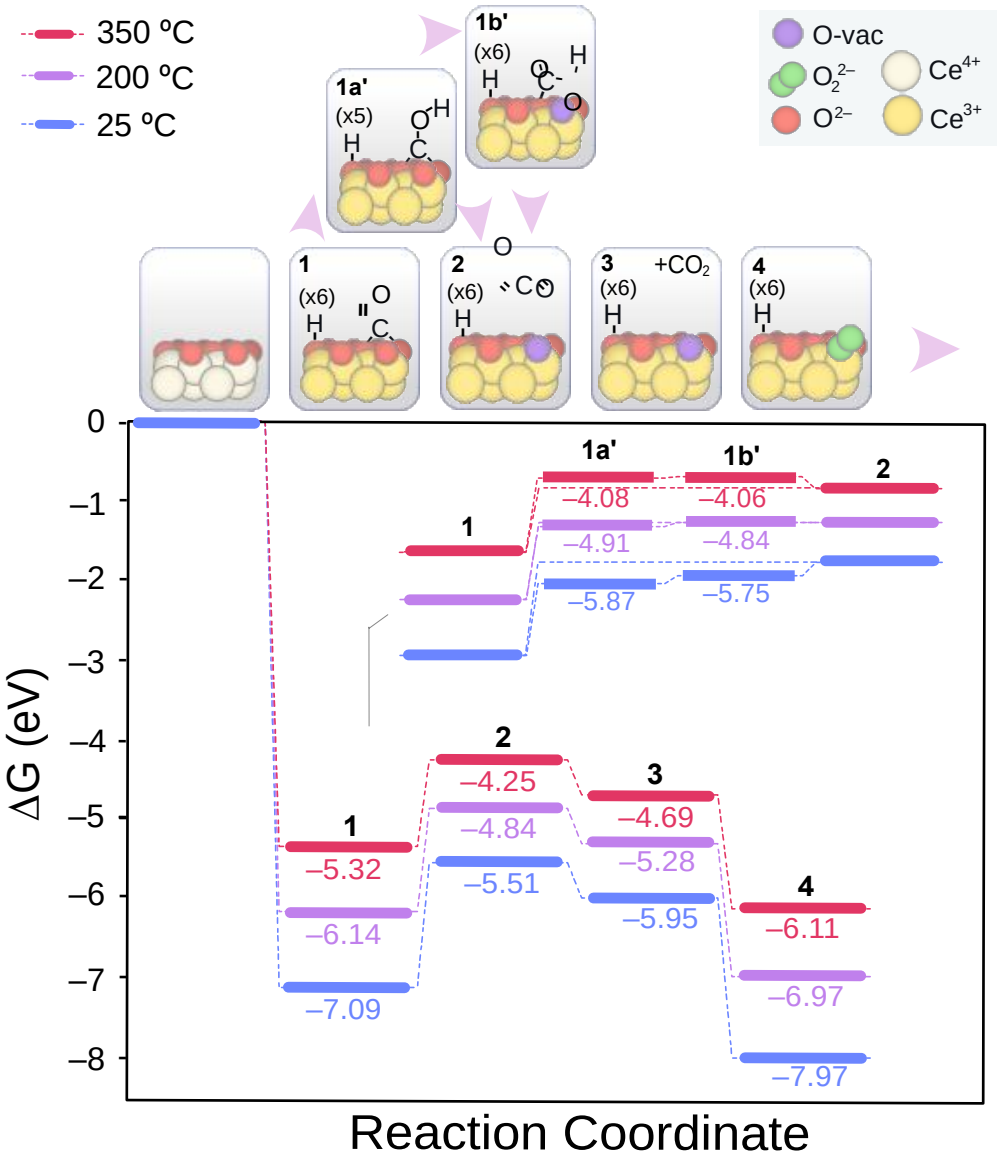

Figure S9. CO oxidation on a CeO_2(110) surface with 6 OH coverage.

Table S1. Energies (ΔE) and Gibbs energies at different temperatures (ΔG^T) from DFT calculations on the modeled $CeO_2(111)$ slab with different adsorbates.

Adsorbate(s) on $CeO_2(111)$	**Binding mode**	**ΔE (eV)**	**$\Delta G^{25\,°C}$ (eV)**	**$\Delta G^{200\,°C}$ (eV)**	**$\Delta G^{350\,°C}$ (eV)**
1 OH	Monocoordinated hydroxyl	–1.25	–0.83	–0.64	–0.48
2 OH		–2.35	–1.52	–1.15	–0.81
3 OH		–3.64	–2.40	–1.84	–1.34
4 OH		–4.83	–3.18	–2.42	–1.76
CO	Top (physisorbed)	–0.18	0.33	0.60	0.83
CO + 2 OH		–2.52	–1.39	–1.12	–0.90
CO + 4 OH		–4.74	–3.00	–2.29	–1.69
CO_2	Tridentated carbonate	–0.46	0.13	0.39	0.60
CO_2 + 2 OH		–3.07	–1.86	–1.12	–0.79
CO_2 + 3 OH		–4.69	–3.18	–2.59	–2.10
CO_2 + V^O		–0.51	0.09	0.35	0.56
CO_2+ 2 OH + V^O		–3.68	–2.47	–1.99	–1.60
CO_2H	Monodentated bicarbonate	–1.32	–0.42	–0.06	0.24
CO_2H + 1 OH	Bidentated bicarbonate	–4.69	–3.18	–2.59	–2.10
CO_2H + 2 OH		–4.08	–2.58	–2.00	–1.51
CO_2H + 3 OH		–5.36	–3.55	–2.86	–2.27
CO_2H + 1 OH + V^O	Bidentated bicarbonate	–3.54	–2.21	–1.77	–1.41
CHO + 1 OH	Bidentated formate	–3.70	–2.46	–1.97	–1.56
CHO + 2 OH		–4.87	–3.33	–2.73	–2.22
CHO + 3 OH		–6.19	–4.33	–3.63	–3.02

Table S2. Energies (ΔE) and Gibbs energies at different temperatures (ΔG^T) from DFT calculations on the modeled CeO_2(110) slab with different adsorbates.

Adsorbate(s) on CeO_2(110)	**Binding mode**	**ΔE (eV)**	**$\Delta G^{25\,°C}$ (eV)**	**$\Delta G^{200\,°C}$ (eV)**	**$\Delta G^{350\,°C}$ (eV)**
1 OH	Linear (hydroxyl A)	–1.55	–1.23	–1.11	–1.00
2 OH		–3.12	–2.48	–2.24	–2.03
3 OH		–4.64	–3.68	–3.32	–3.01
4 OH		–6.19	–4.90	–4.43	–4.01
5 OH	Linear + tilted (hydroxyl B)	–6.91	–5.30	–4.71	–4.19
6 OH		–7.66	–5.73	–5.02	–4.40
7 OH		–8.12	–5.86	–5.04	–4.31
8 OH		–8.82	–6.25	–5.30	–4.47
CO	Bidentate carbonate	–3.66	–2.93	–2.68	–2.49
CO + 3 OH		–7.89	–5.89	–5.30	–4.81
CO + 6 OH		–9.75	–7.09	–6.14	–5.32
CHO + 2 OH	Bicarbonate bidentate (A)	–6.65	–4.93	–4.32	–3.81
CHO + 5 OH		–7.97	–5.93	–5.21	–4.59
CHO + 2 OH	Bicarbonate monodentate (B)	–6.26	–4.62	–4.06	–3.60
CHO + 5 OH		–7.50	–5.53	–4.86	–4.29
CO_2	Monodentate carbonate	–1.31	–0.70	–0.44	–0.32
CO_2 + 3 OH		–6.92	–5.03	–4.29	–3.76

Table S3. Energies (ΔE) and Gibbs energies at different temperatures (ΔG^T) from DFT calculations on the modeled CeO_2(100) slab with different adsorbates.

Adsorbate(s) on CeO_2(100)	**Binding mode**	**ΔE (eV)**	**$\Delta G^{25\,°C}$ (eV)**	**$\Delta G^{200\,°C}$ (eV)**	**$\Delta G^{350\,°C}$ (eV)**
1 OH	Monocoordinated hydroxyl[‡]	–1.82	–1.51	–1.40	–1.31
2 OH		–3.57	–2.96	–2.74	–2.55
3 OH		–5.01	–4.09	–3.77	–3.49
4 OH		–6.38	–5.17	–4.73	–4.36
CO	Bridge (physisorbed)	–0.32	0.20	0.53	0.83
CO + 4 OH		–6.35	–4.61	–3.85	–3.18
CO_2	Polydentate carbonate	–1.96	–1.34	–1.07	–0.86
CO_2 + 3 OH		–7.23	–5.72	–5.13	–4.63
CO_2H	Monodentate bicarbonate	–2.01	–1.22	–0.88	–0.60
CO_2H + 2 OH		–5.28	–3.80	–3.24	–2.77