Ni on the CeO_2(110) and (100) Surfaces: Adsorption vs. Substitution Effects on the Electronic and Geometric Structures and Oxygen Vacancies

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Supplementary Information

		a (Å)	*b* (Å)	*c* (Å)	Δ (eV)
CeO_2	Expt.	5.411	5.411	5.411	2.60-3.90[1]
	PBE	5.413	5.413	5.413	1.96
	PBE+U	5.439	5.439	5.439	2.32
Ce_2O_3	Expt.	3.891	3.891	6.059	2.40[1]
	PBE	3.783	3.783	6.022	0.00
	PBE+U	3.830	3.830	6.010	2.31
NiO	Expt.	5.105	5.105	5.105	4.20[2]
	PBE	5.056	5.056	5.056	0.69
	PBE+U	5.104	5.104	5.104	2.93

Table T1: Lattice parameters and electronic band gaps obtained from DFT/PBE, DFT/PBE+U and their comparison to experimental data.

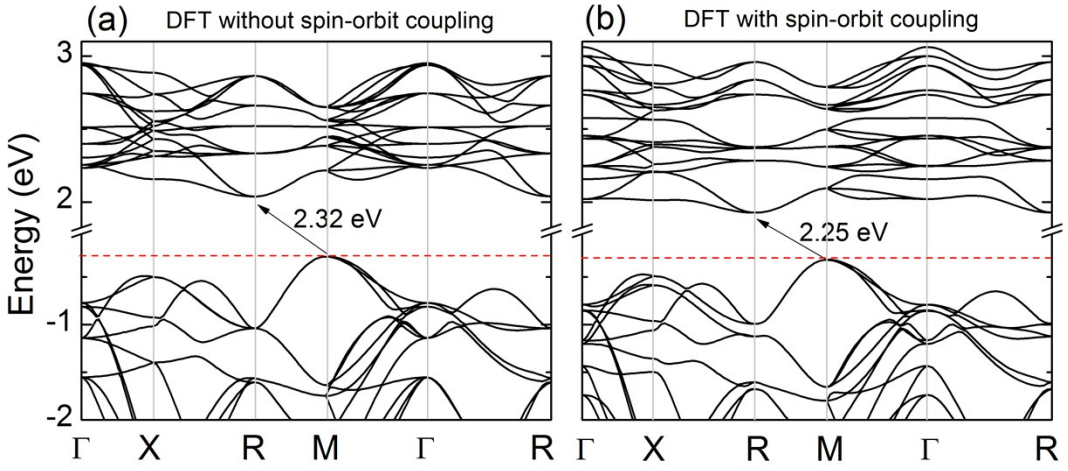

Figure S1. Calculated band structures of pure CeO_2 (a) without and (b) with spin-orbit coupling. The arrows indicate the fundamental band gap. The horizontal dashed lines indicate the top of valence bands.

1. Ni-adsorbed, Ni-substituted (110) surface and the formation of oxygen vacancies.

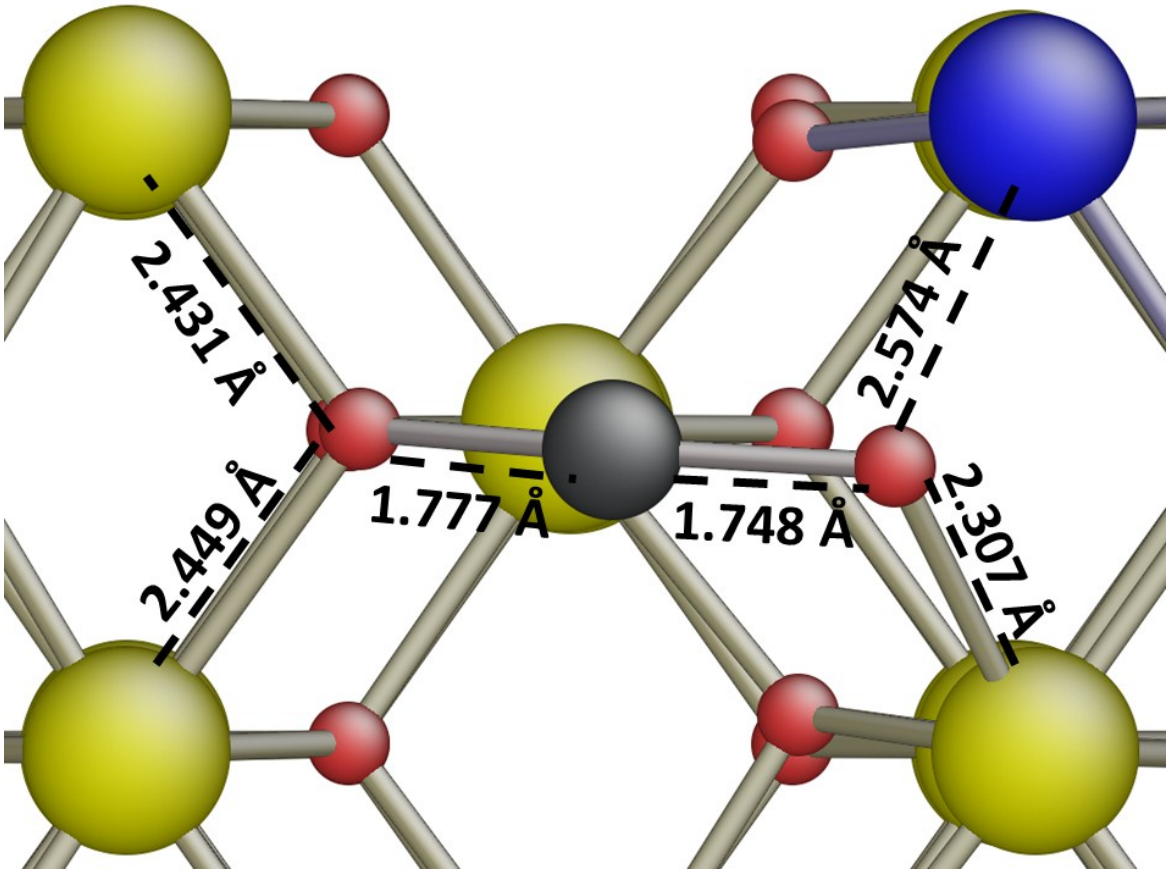

Figure S2: Bond distances surrounding the Ni^{+} adsorbate on a bridge site on the CeO_2 (110) surface. Ce^{3+} ion is blue, Ce^{4+} ion is yellow, O^{2-} ion is red and Ni^{+} ion is gray.

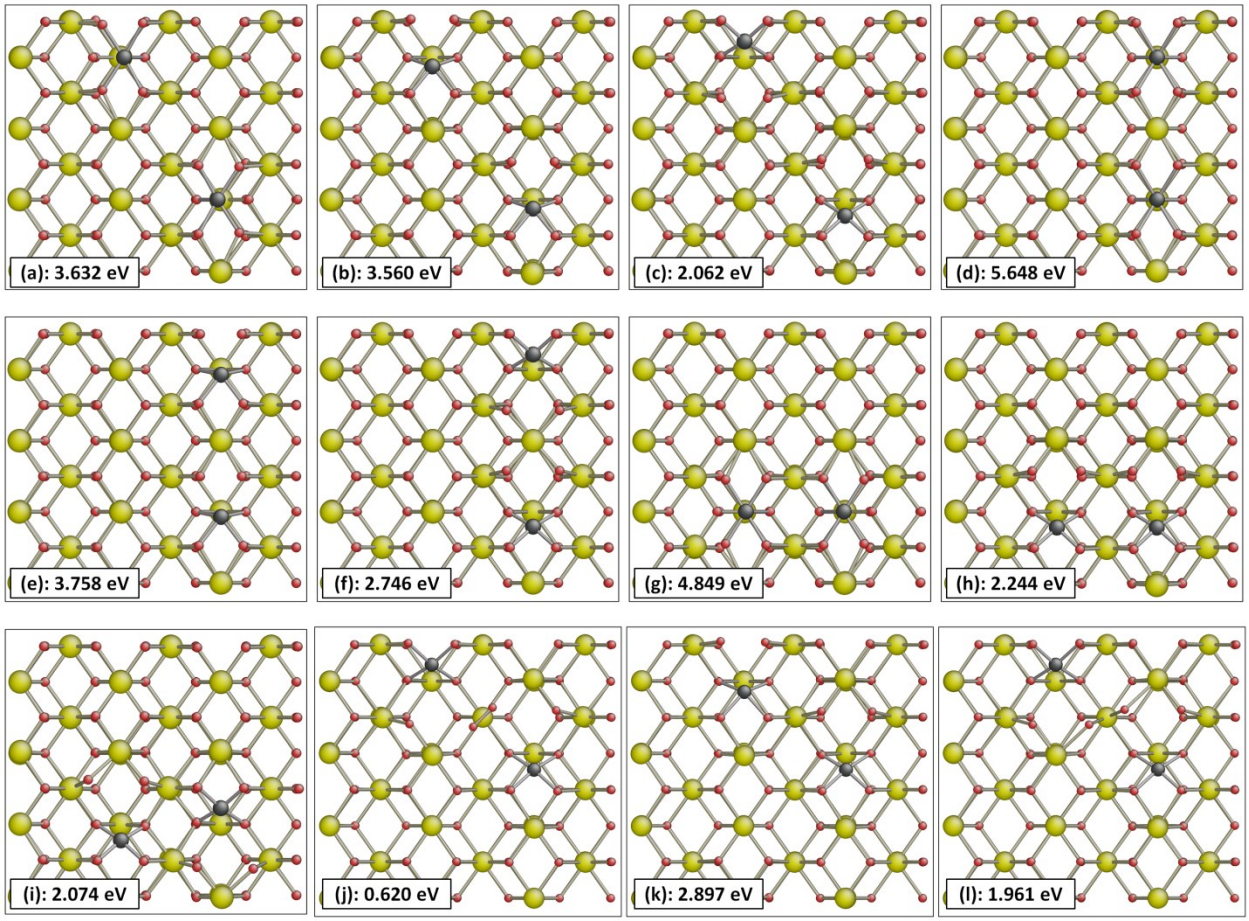

Figure S3: Metastable configurations for various distributions of two Ni substituents on the CeO_2 (110) surface. The energies are reported with respect to the most stable distribution of two Ni substituents on the CeO_2 (110) surface shown in figure 7(b) of the main text. Ce atoms are yellow, O atoms are red, Ni atoms are gray.

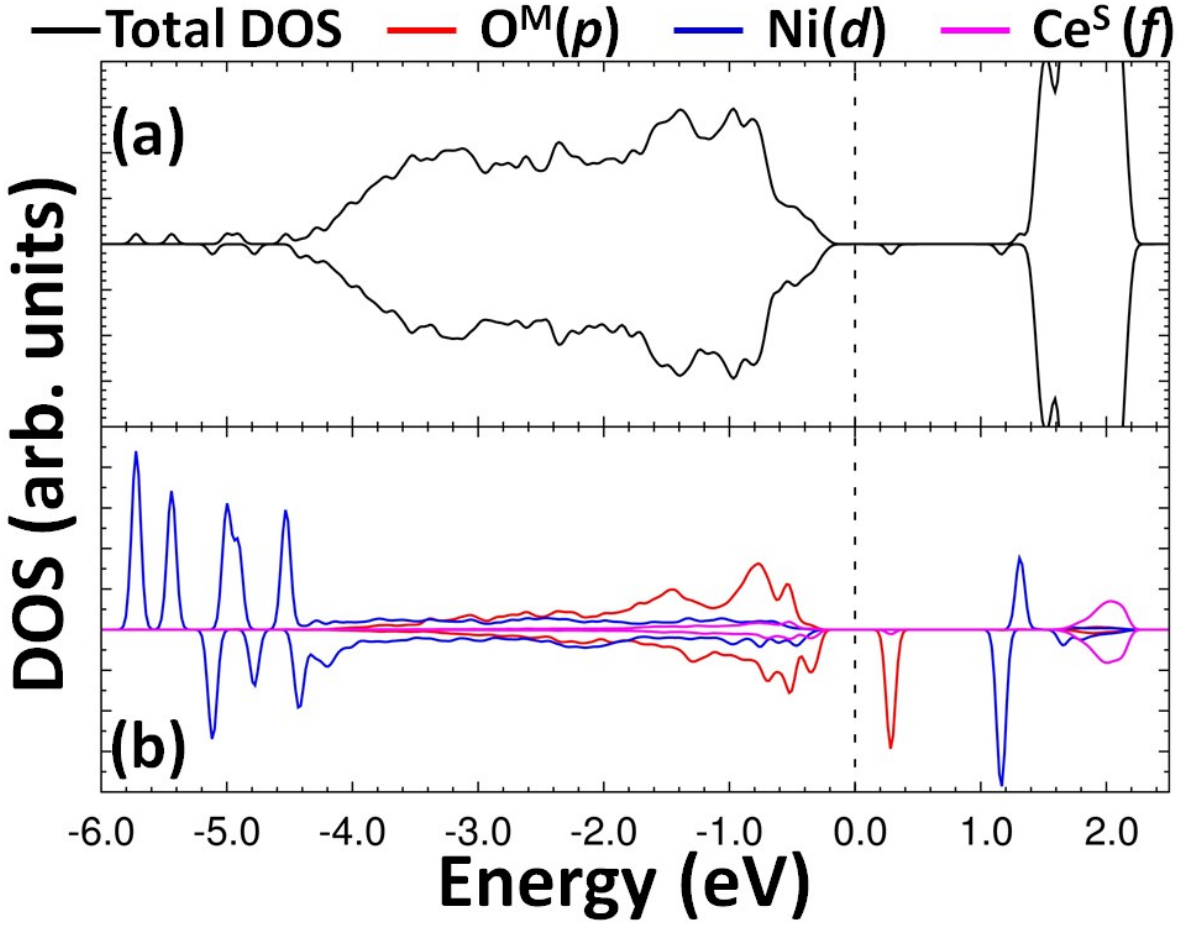

Figure S4: (a) Total and (b) projected density of states for mono-Ni substituent on the CeO_2 (110) surface. O^M, Ce^S, and Ni correspond to the surface Oxygen, Cerium and Nickel atoms referenced in figure 7(a) of the main text.

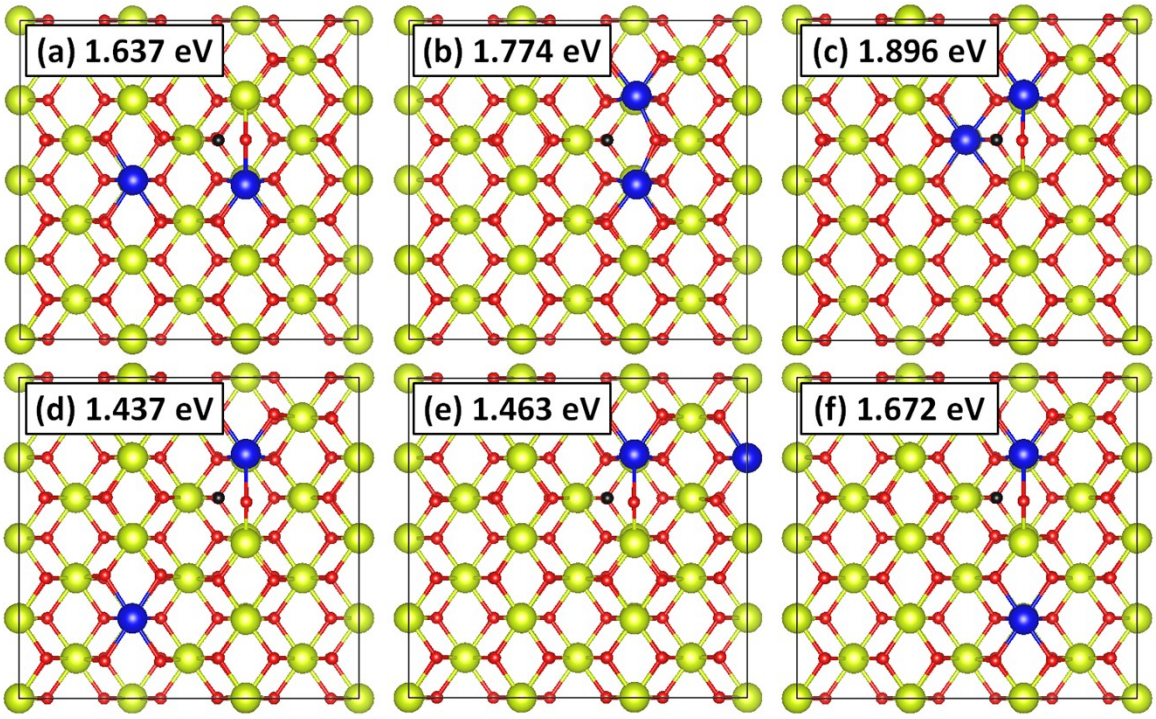

Figure S5: Active oxygen vacancy formation on CeO_2 (110) surface. The formation energies in panels (a) to (f) are computed using equation (6) in the main text. Ce^{3+} ion is blue, Ce^{4+} ion is yellow, O^{2-} ion is red and the oxygen vacancy position is indicated by a black sphere.

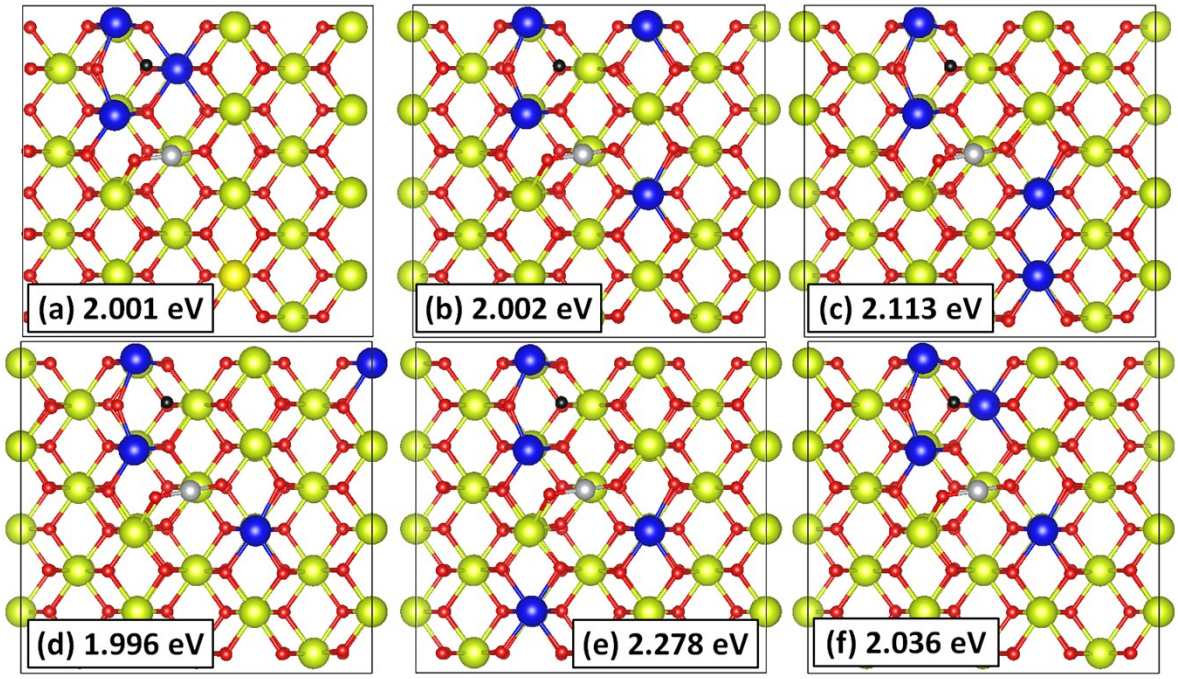

Figure S6: Active oxygen vacancy formation on Ni adsorbed CeO_2 (110) surface. The formation energies in panels (a) to (f) are computed using equation (7) in the main text. Ce^{3+} ion is blue, Ce^{4+} ion is yellow, O^{2-} ion is red, Ni^{+}/Ni^{2+} ion is grey and the oxygen vacancy position is indicated by a black sphere. Ni is in its Ni^{+} oxidation state in panel (a) and Ni^{2+} oxidation state in panels (b) to (f).

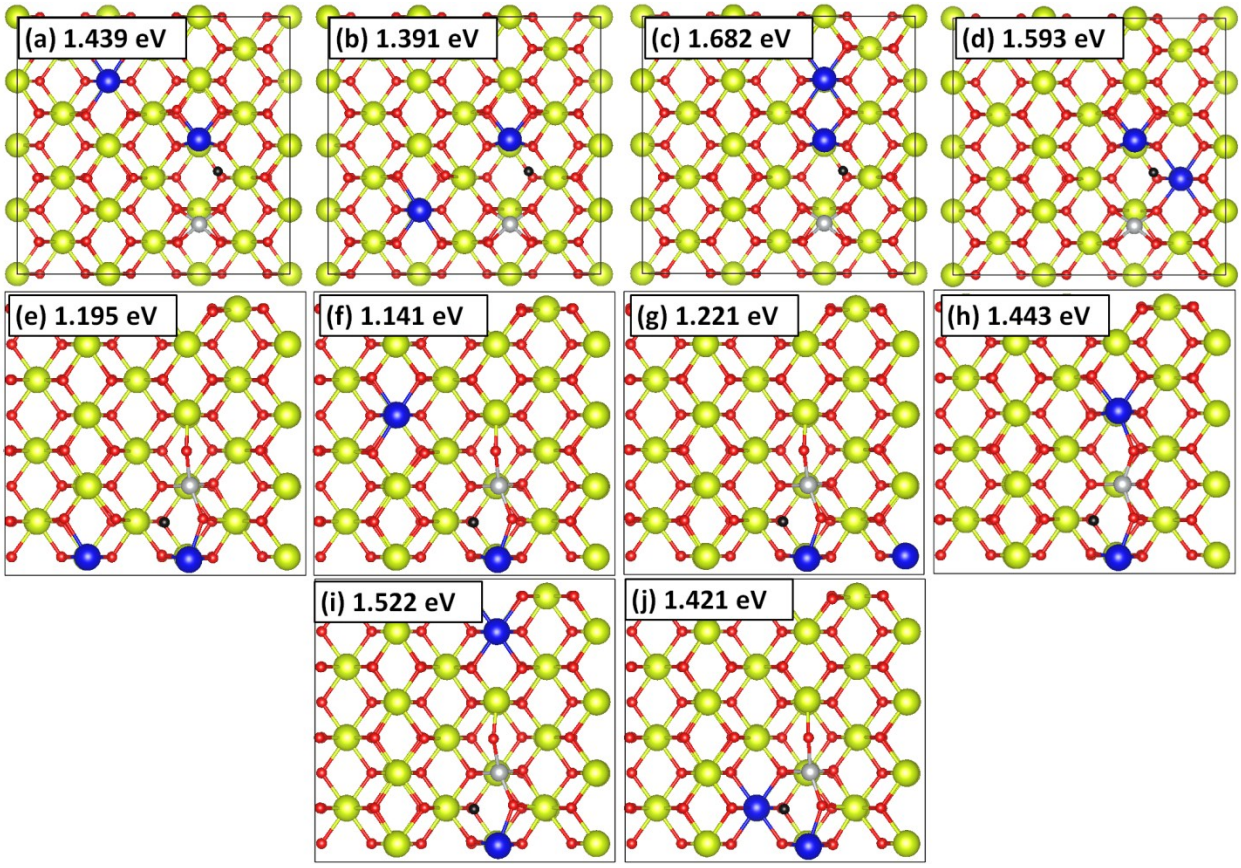

Figure S7: Active oxygen vacancy formation on the mono-Ni substituted CeO_2 (110) surface. The formation energies in panels (a) to (j) are computed using equation (8) in the main text. Ce^{3+} ion is blue, Ce^{4+} ion is yellow, O^{2-} ion is red, Ni^{2+} ion is grey and the oxygen vacancy position is indicated by a black sphere.

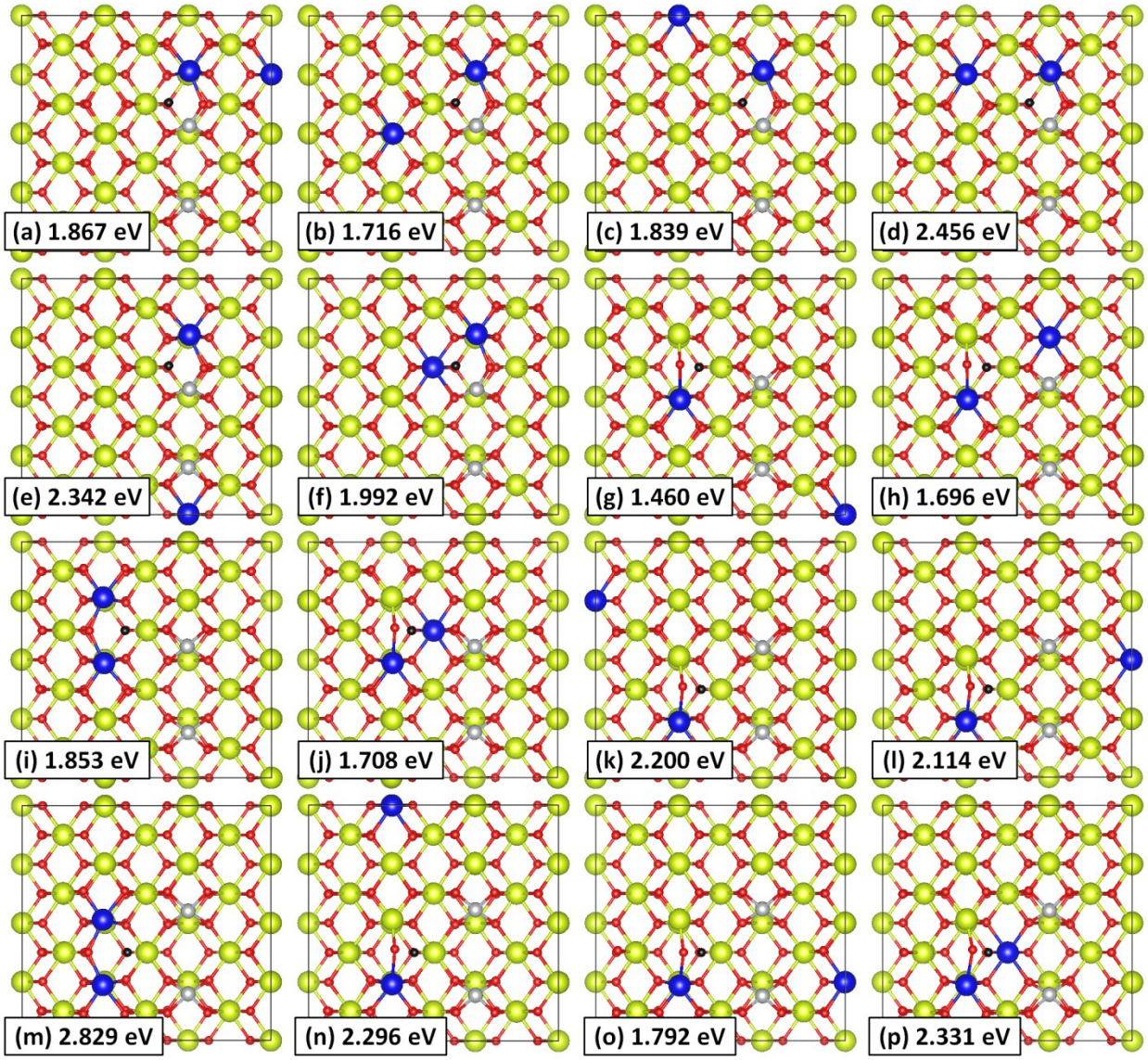

Figure S8: Active oxygen vacancy formation on the di-Ni substituted CeO_2 (110) surface. The formation energies in panels (a) to (p) are computed using equation (8) in the main text. Ce^{3+} ion is blue, Ce^{4+} ion is yellow, O^{2-} ion is red, Ni^{2+} ion is grey and the oxygen vacancy position is indicated by a black sphere.

2. Ni-adsorbed, Ni-substituted (100) surface and the formation of oxygen vacancies

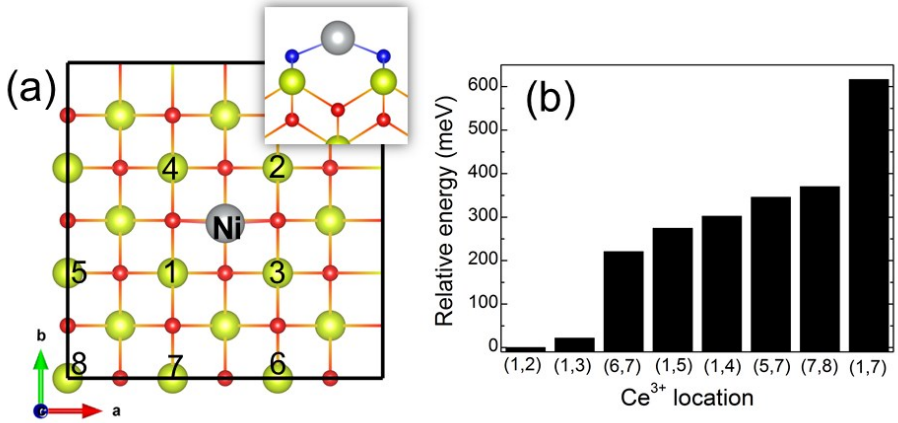

Figure S9 (a) Initial configuration for Ni adsorbed on the CeO_2 (100) surface. The numbers indicate the possible positions of the two Ce^{3+} ions. Yellow – cerium, red and blue – oxygen, grey – nickel. (b) The relative energy for different locations of Ce^{3+} pair as shown in panel (a). All of the values are referred to the most stable configuration of two Ce^{3+} ions located at sites 1 and 2 in panel (a).

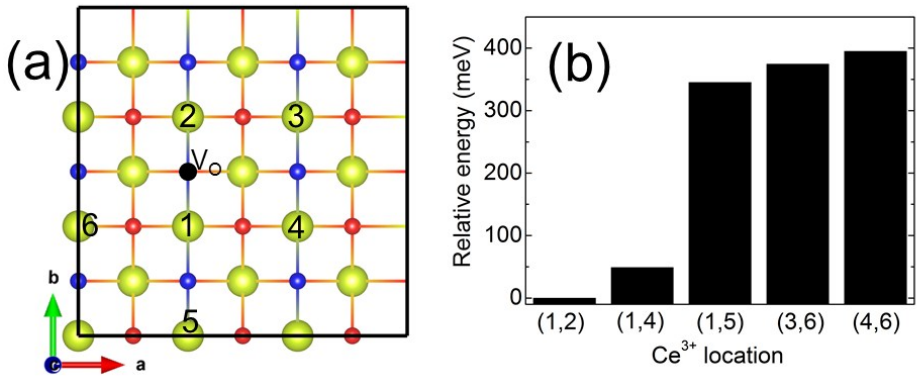

Figure S10 (a) Initial configuration for the oxygen vacancy on CeO_2 (100) surface. The numbers indicate the possible positions of the two Ce^{3+} ions. Yellow – cerium, red and blue – oxygen, black – oxygen vacancy. (b) The relative energy for different locations of the Ce^{3+} pair. All the values are referred to the most stable configuration of two Ce^{3+} ions, where Ce^{3+} ions are located at positions 1 and 2 as shown in panel (a).

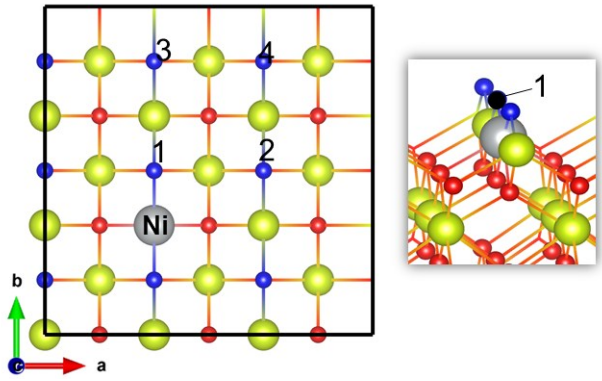

Figure S11 The initial configuration for a single Ni-substituted CeO_2 (100) surface with a charge compensating oxygen vacancy. The numbers indicate the possible positions of vacancy. The inset is the side view. Yellow – cerium, red and blue – oxygen, grey – nickel, black – oxygen vacancy.

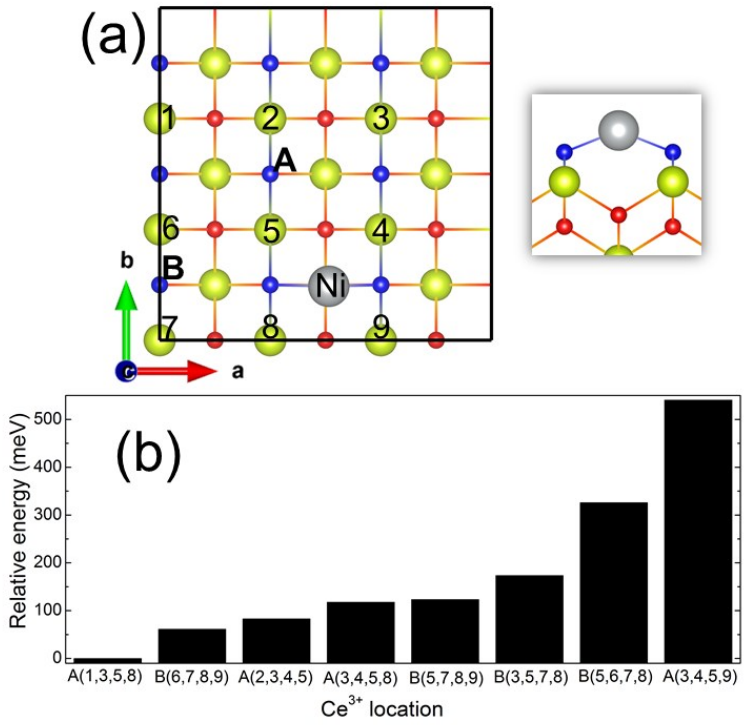

Figure S12 (a) The initial configuration for a single Ni-adsorbed CeO_2 (100) surface with an active oxygen vacancy. A and B mark the position of the considered vacancy. The numbers indicate the considered positions of the four Ce^{3+} ions induced by the adsorbed Ni and the oxygen vacancy at position A or B. Yellow – cerium, red and blue – oxygen, grey – nickel. The inset is the side view. (b) The relative energy of possible distributions for the four Ce^{3+} ions as indicated by the number and letter (A or B) in panel (a). The symbol A(1,3,5,8) means oxygen vacancy at position A and four Ce^{3+} ions at sites 1, 3, 5 and 8 in panel (a). All of the values are referred to the most stable configuration A(1,3,5,8).

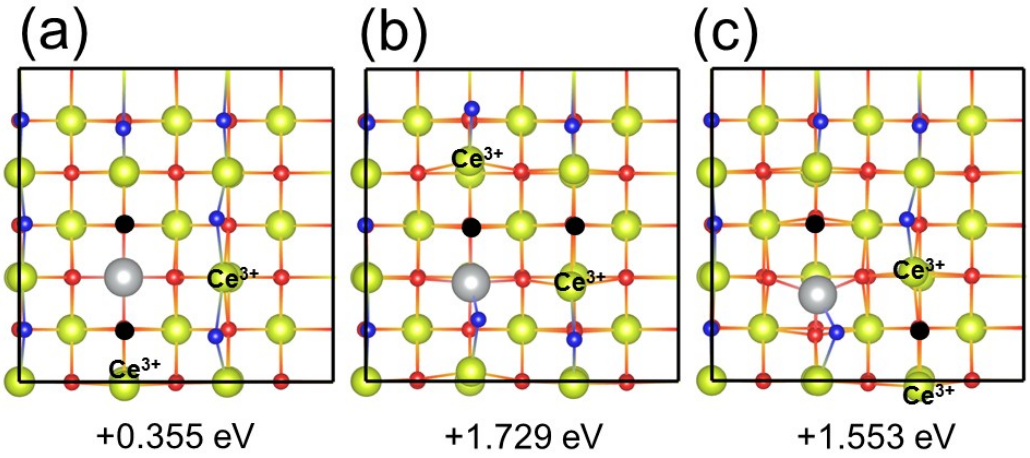

Figure S13 The optimized atomic structure of the Ni-substituted CeO_2 (100) surface with two oxygen vacancies to simulate the formation of "active vacancy". Panels (a), (b) and (c) show three different configurations. Yellow – cerium, red and blue – oxygen, grey – nickel, black – oxygen vacancy. The numbers are the formation energy of the active O vacancy.

3. Ni-adsorbed, Ni-substituted (111) surface and the formation of oxygen vacancies

Here, we have considered the (111) surface of CeO_2, as shown below. Stoichiometric (111) slabs with a (3×3) expansion of the oxygen-terminated surface unit cell that includes 15 atomic layers (45 CeO_2 units) was used in the calculations.

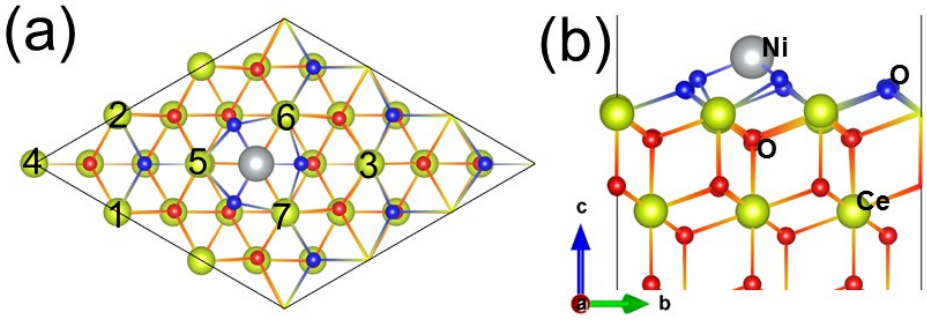

Figure S14 (a) The optimized atomic structures of Ni adsorbed CeO_2 (111) surface with two Ce^{3+} ions at 1 and 2 sites and the other numbers indicate the possible positions of the two Ce^{3+} ions. (b) The optimized atomic structure of the Ni-adsorbed CeO_2 (111) surface in side view. Yellow – cerium, red and blue – oxygen, grey - nickel.

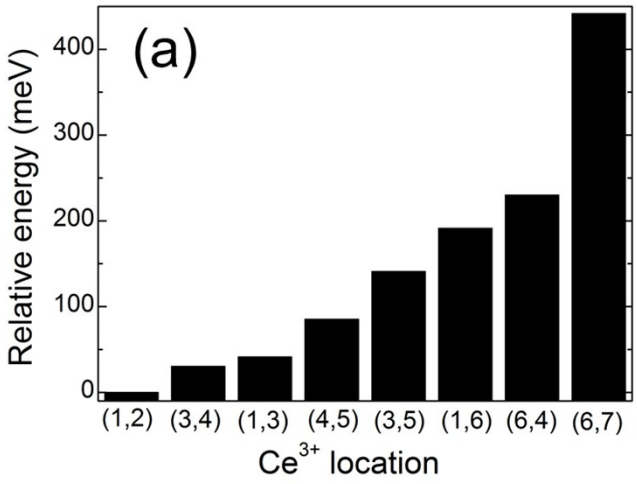

Figure S15 The relative energy of possible distributions for the two Ce^{3+} ions as indicated by the number in Figure S14 (a). The symbol (1,2) means two Ce^{3+} ions at sites 1 and 2. All of the values are referred to the most stable configuration (1,2).

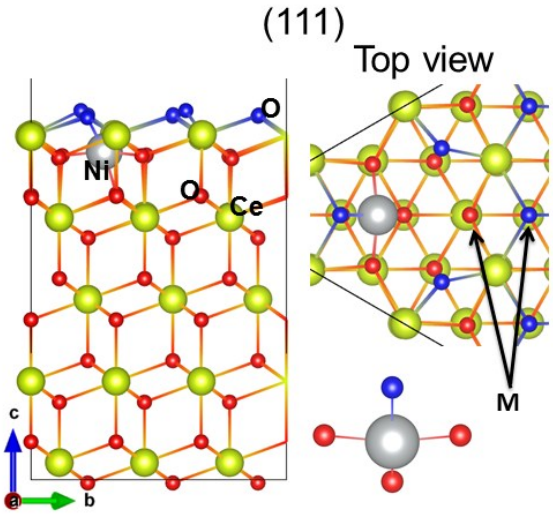

Figure S16 The optimized atomic structures of Ni substituted CeO_2 (111) surface in side (left panel) and top (right-up panel) view. Right-down panel shows the local structure surrounding the Ni dopant. Yellow – cerium, red and blue – oxygen, grey - nickel. Letter M indicates the magnetic oxygen atoms.

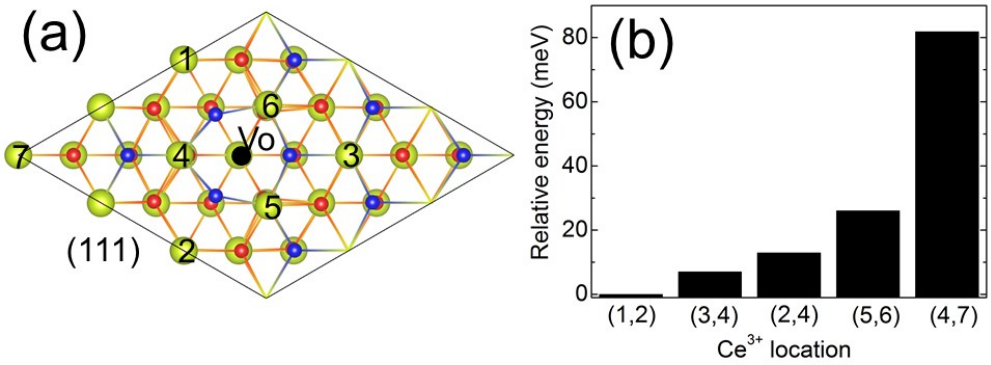

Figure S17 (a) The optimized atomic structure of an oxygen vacancy on CeO_2 (111) surface with two Ce^{3+} ions at 1 and 2 sites and the other numbers indicate the possible position of the two Ce^{3+} ions. (b) The relative energy for different locations of Ce^{3+} pair. All of the values are referred to the most stable configuration of two Ce^{3+} ions, located at positions 1 and 2 in Figure S17 (a).

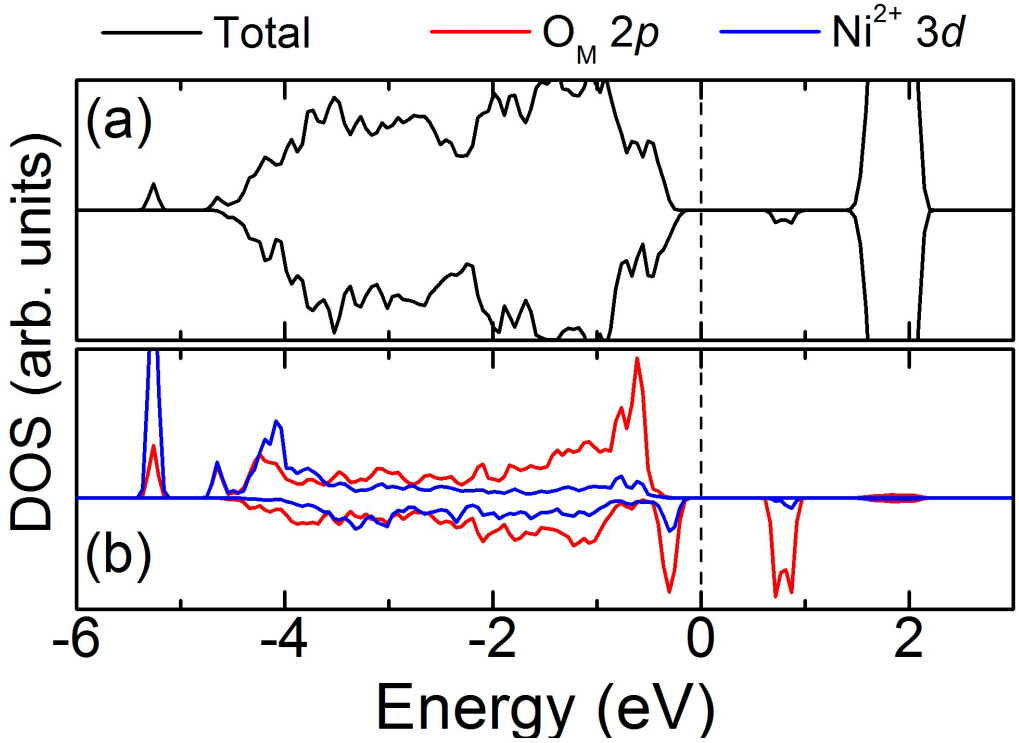

Figure S18. The total density of states (DOS) in the upper panel and the projected DOS of magnetic O 2*p* (O_M) and Ni^{2+} 3*d* orbitals in the lower panel. The curves above (below) the horizontal axis correspond to spin-up (down) states. The Fermi level (the vertical dashed line) is set to zero.

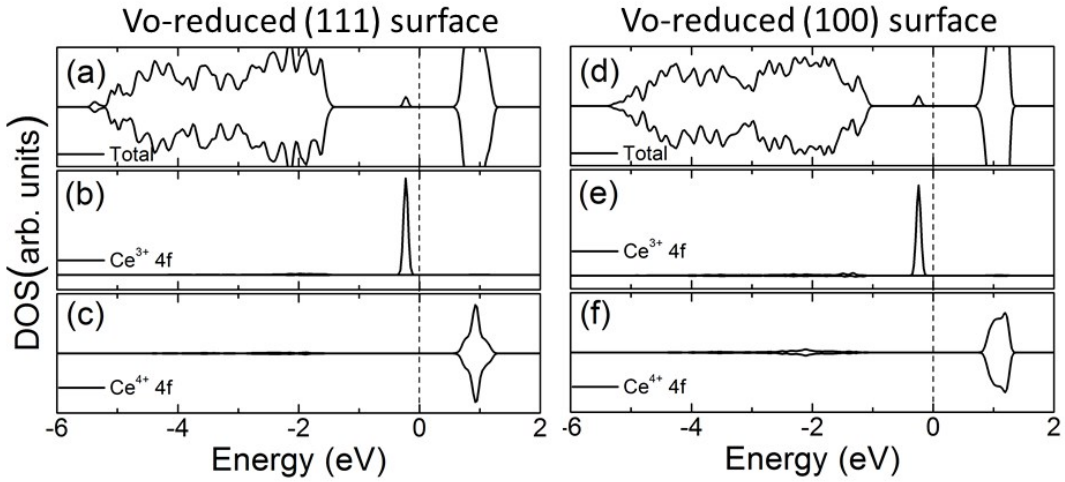

Figure S19 (a) and (d): Total density of states (DOS). (b) and (e): Projected DOS of Ce^{3+} 4*f*. (c) and (f): Ce^{4+} 4*f* orbitals for the most stable configuration of oxygen vacancies on (100) and (111) surfaces. The curves above (below) the horizontal axis correspond to spin-up (down) states. The Fermi level (the vertical dashed line) is set to zero.

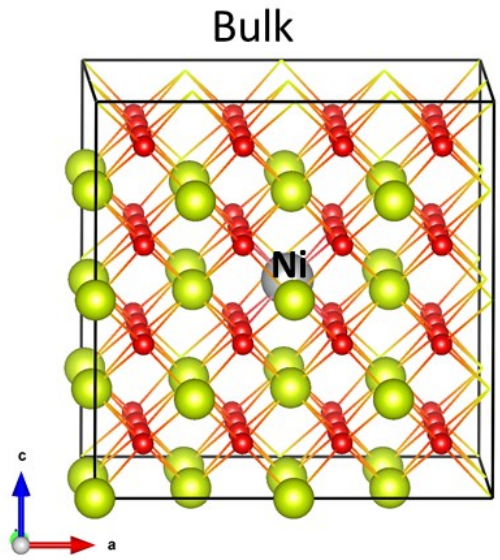

Figure S20 The optimized atomic structure of a Ni substituent in the supercell with 96 atoms. Yellow – cerium, red– oxygen, grey - nickel.

Surface	E_{Niads}	E_{Nif}	E_{Vof}^{p}
(100)	-1.490	-1.735	+1.679
(111)	-0.185	-0.572	+1.983

Table T2. The calculated adsorption energy (E_{Niads}) (eV) of a Ni adatom, the formation energy of a Ni substituent (E_{Nif}) and an oxygen vacancy (E_{Vof}^{p}) on (100) and (111) surfaces by following equation (1), (2) and (5) in the main text of the article. The detailed atomic structure based on the (111) surface can be found in supporting information.

References

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R. Zimmermann, P. Steiner, R. Claessen, F. Reinert, S. Hüfner, P. Blaha and P. Dufek, *J. Phys.: Condens. Matter*, 1999, 11, 1657.