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

Supplementary Information

A DFT+U study of NO evolution at reduced CeO_2 (110)

Jie Zhang[ab], Xue-Qing Gong[ab*] and Guanzhong Lu[a*]

[a] *Key Laboratory for Advanced Materials and Research Institute of Industrial Catalysis, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P.R. China*

[b] *State Key Laboratory of Chemical Engineering and Centre for Computational Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, P.R. China*

[*] *Corresponding authors: xgong@ecust.edu.cn, gzhlu@ecust.edu.cn*

1. Calculation details

All calculation were performed with the GGA-PW91 functional using the Vienna ab initio simulation package (VASP) code[s1-3]. The valence electronic states of Ce (4*f*, 5*s*, 5*p*, 6*d*, 6*s*), O (2*s*, 2*p*) and N (2*s*, 2*p*) were described by plane-wave basis sets with the cut-off energy at 400 eV, and core-valence interactions were treated with the projector augmented wave (PAW) method[s4]. To correctly describe the localization of Ce 4*f* electrons, the DFT+U methodology was used, where U=5 eV was applied[s5-7]. The transition states (TS) of surface reactions were determined by the constrained minimization method[s8, 9] and electron charge analyses were performed by Bader decomposition of charge density[s10].

The CeO_2(110) surface was modeled as periodic slab with five CeO_2 layers, and the bottom two layers were fixed while the other layers were allowed to relax during all the calculations. The force threshold of all the relaxed atoms was set to 0.02 eV/Å and spin polarization was also considered. The vacuum height between slabs was ~15 Å in order to eliminate the interaction between the neighboring slabs. CeO_2(110) surface was built by a 2×3 supercell (see Fig. 1), and the *k*-point mesh was set to 2×2×1 in the calculations.

In this work, the single oxygen vacancy formation energy was determined by the following expression:

$$E_v^f = E_{vCeO_2} + \frac{1}{2}E_{O_2} - E_{CeO_2}$$

Where E_{vCeO_2} is the total energy of CeO_2(110) with a single O_v, E_{O_2} is total energy of O_2 in gas phase and E_{CeO_2} is the total energy of stoichiometric CeO_2(110) surface.

We also studied the oxygen vacancies pair formation energy of CeO_2(110) by the following expression:

$$E_{vpair}^f = E_{biO_v pair} + E_{O_2} - E_{CeO_2}$$

Where $E_{biO_v pair}$ is the total energy of CeO_2(110) surface with two oxygen vacancies.

To determine the adsorption energies (E_{ad}) of NO at stoichiometric and reduced CeO_2(110), we used the following equation:

$E_{ad} = -(E_{NO/CeO_2} - E_{NO} - E_{CeO_2})$ for stoichiometric $CeO_2(110)$ surface

where E_{NO/CeO_2} is the total energy of the interacting system with NO at clean CeO_2 surface and E_{NO} is the total energy of NO molecule in gas phase;

and $E_{ad} = -(E_{NO/vCeO_2} - E_{NO} - E_{vCeO_2})$ for reduced $CeO_2(110)$ surface

where $E_{NO/vCeO_2}$ is the total energy of the interacting system between NO and reduced CeO_2 surface.

2. NO_x adsorption at stoichiometric and reduced $CeO_2(110)$

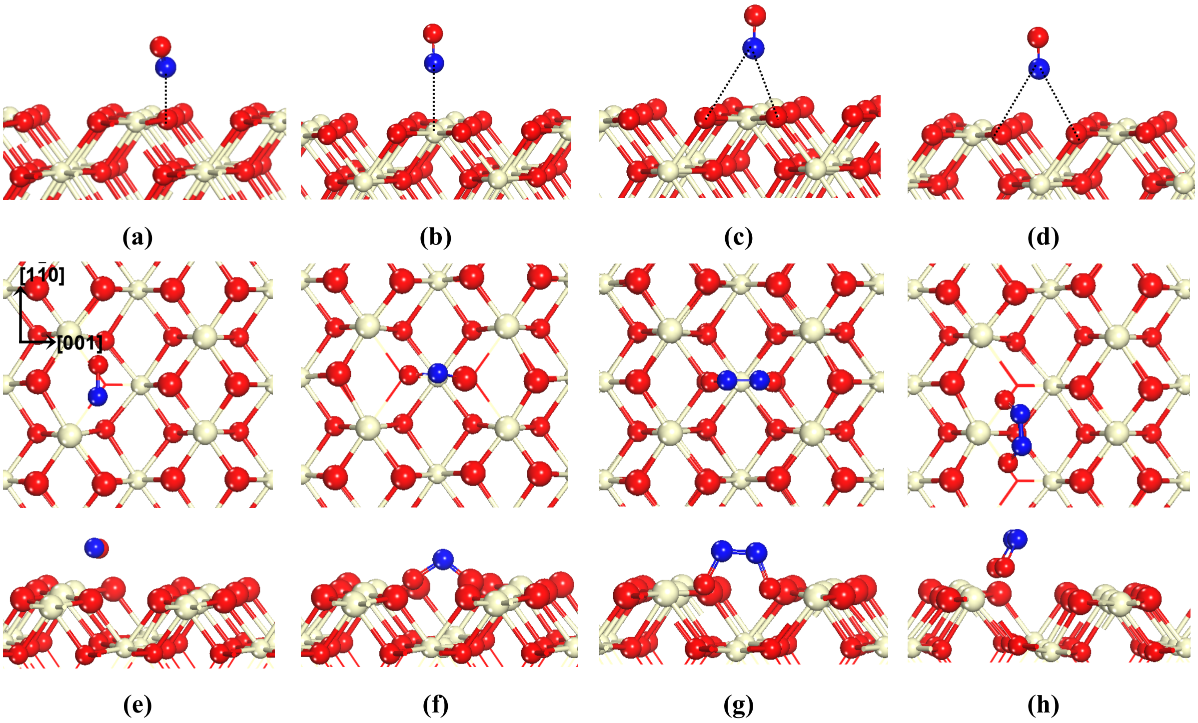


Fig. S1 Calculated single NO adsorption on (a: O_{3c}; b: Ce_{6c}; c: O_A-O_C site and d: O_A-O_B site) of stoichiometric and (e: atop; f: NO_2 formation with neighboring O_{3c}) defected $CeO_2(110)$ surface with O vacancy, and N_2O_2 dimer adsorption at defected $CeO_2(110)$ surface with two O vacancies (g: O_{Av}-O_{Bv} and h: O_{Av}-O_{Dv}). In figures (e)-(h), the upper are top views and the bottom are side views. Ce is in white, O in red and N in blue.

3. Formation energies of single oxygen vacancies and oxygen vacancy pairs (E_v^f) on $CeO_2(110)$

Table S1. Calculated oxygen vacancy formation energies and structural paremeters on CeO$_2$ (110).

	O$_v$ site	Single E_v^f /eV	Split E_v^f /eV	O-O distance /Å
Single O$_v$	O$_A$	1.87	1.71	
O$_v$ pair	O$_A$-O$_B$	4.81	4.50	2.78
	O$_A$-O$_C$	5.22	/	2.58
	O$_A$-O$_D$	3.96	3.62	3.79
	O$_A$-O$_E$	3.52	3.24	4.70

4. Oxygen vacancy diffusion

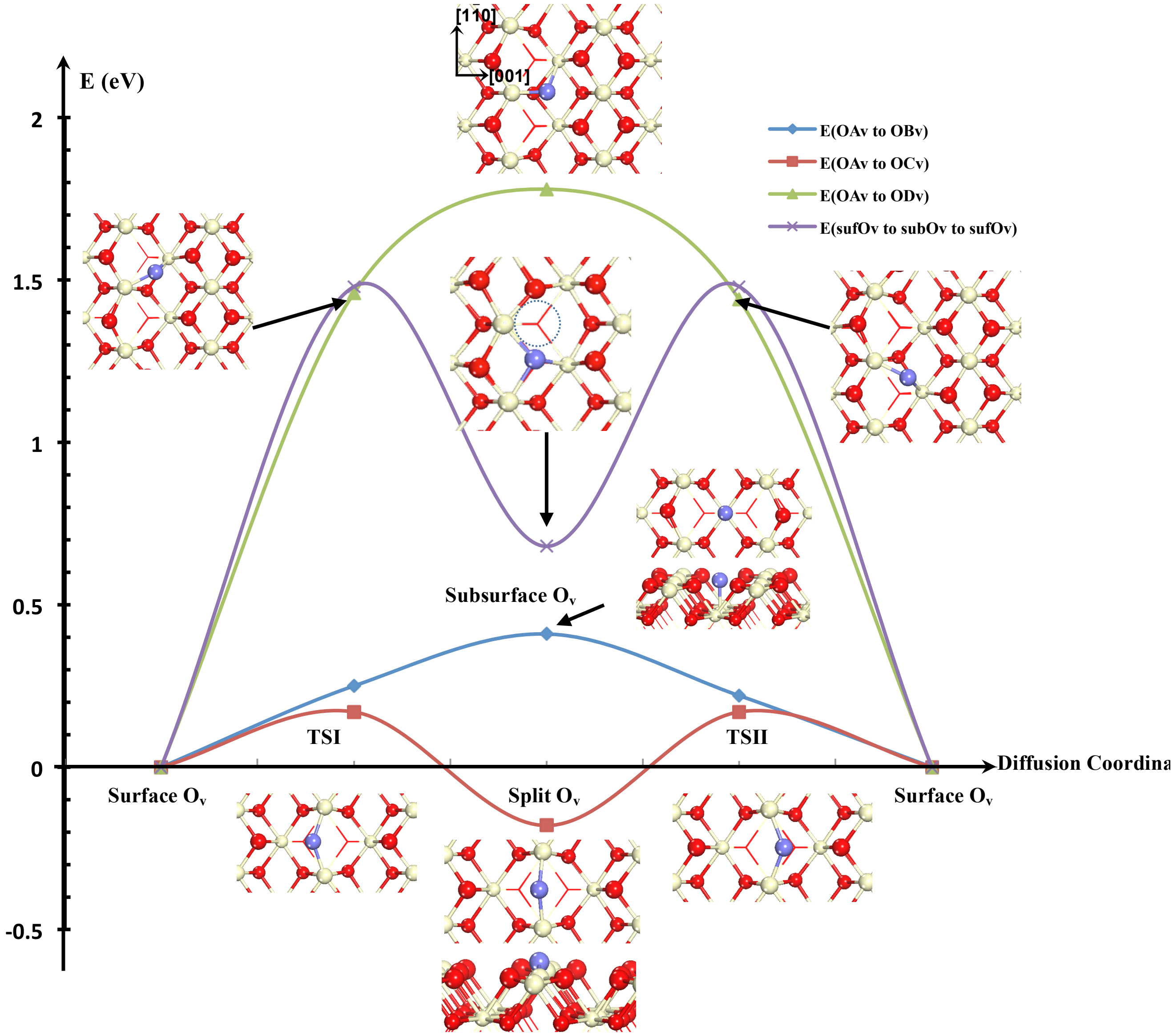
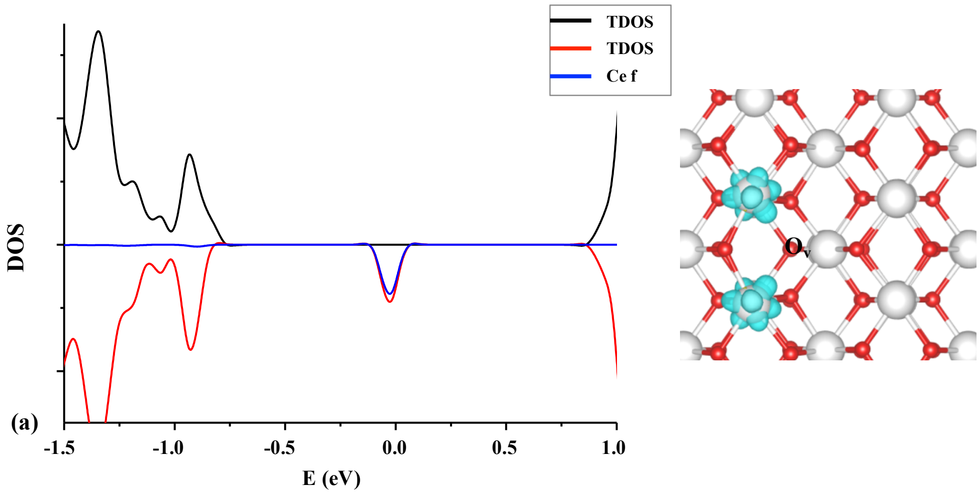
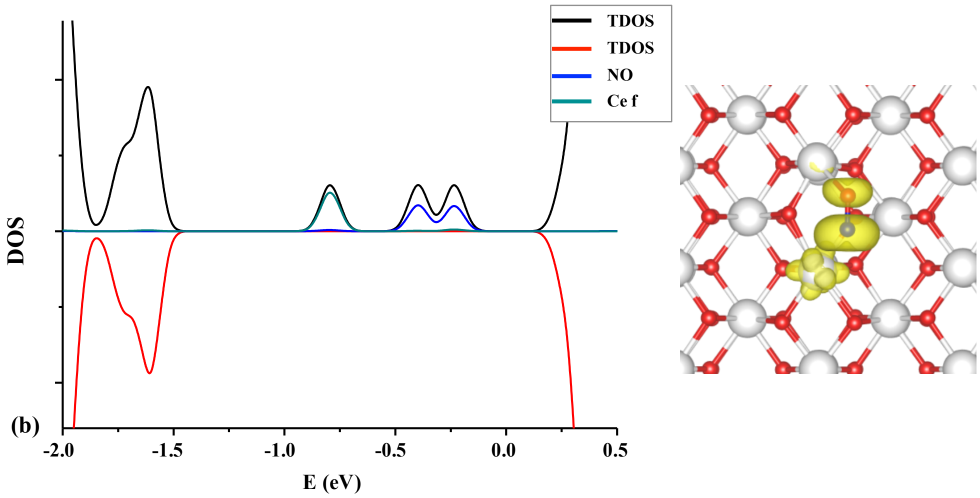
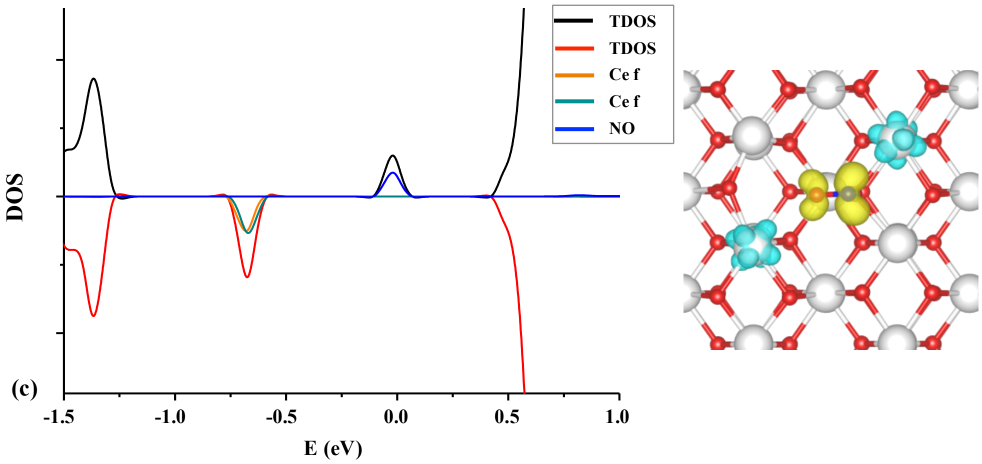


Fig. S2 Calculated energy profiles and key states of O atom diffusion on defected CeO$_2$(110) (diffusing O is in purple).

5. Electronic structure analyses







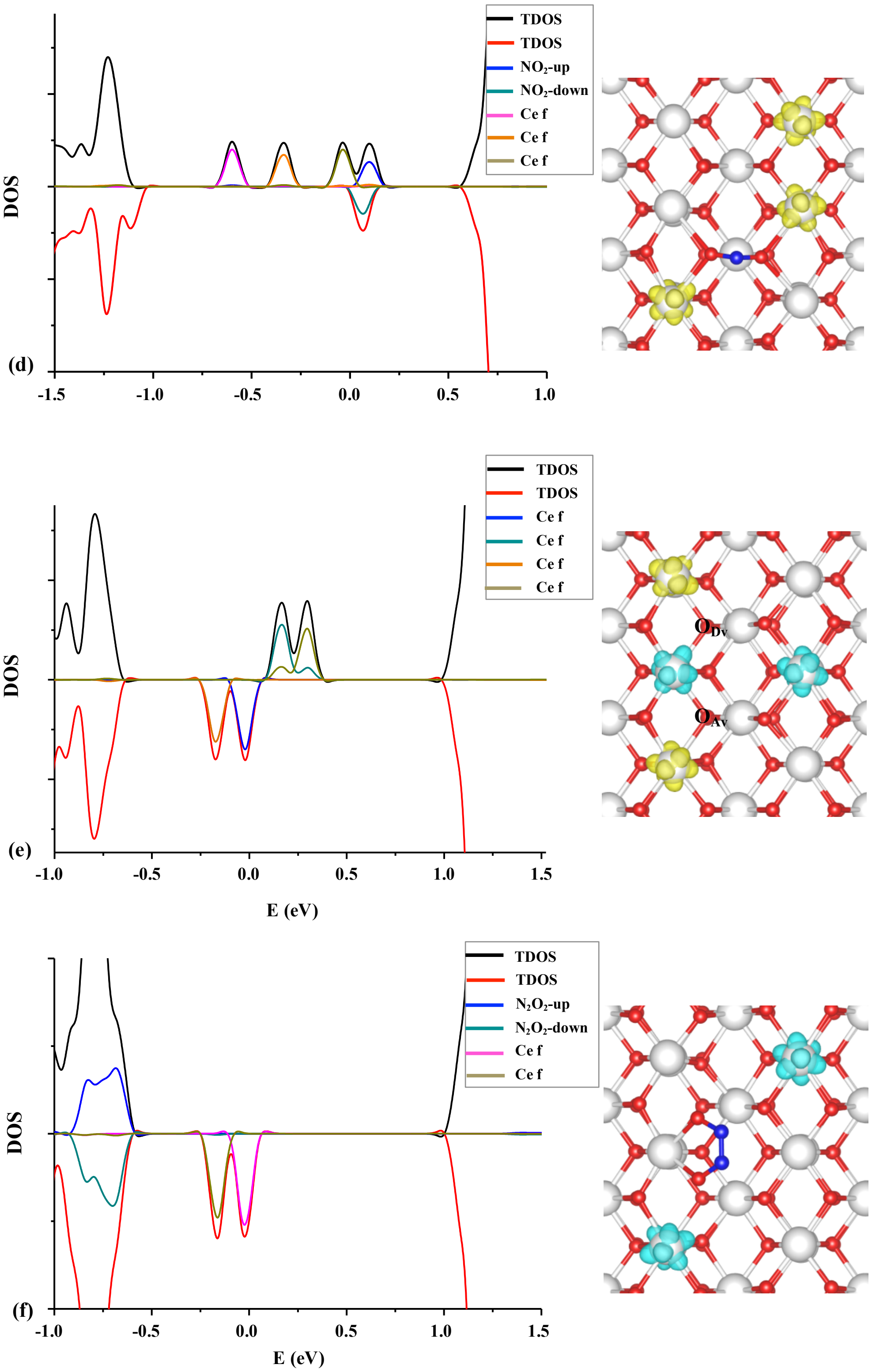


Fig. S3 Calculated density of states (DOS) and localized spin electron isosurfaces of (a) vacancy, and (b) NO adsorption, (c) the TS state of NO oxidized to NO_2 and (d) NO_2 adsorption on single O vacancy, and (e) O_A-O_D vacancy pair and (f) N_2O_2 adsoption on O vacancy pair. The spin up electronic density is shown in light yellow and the spin down is shown in light blue in electron isosurfaces picture. The spin-up and spin-down states of TDOS are plotted by black and red lines respectively.

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