Supporting Information

Role of Oxygen Vacancies in the Surface Evolution of H at CeO₂(111): A Charge Modification Effect

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Fig. S1 Calculated route of H bulk diffusion (via O in black) from top surface O atom (O-1) to O-5 at the 7th atomic layer (12 atomic layers in total). Some specific atoms are illustrated on the right.

Table S1 Calculated formation energies of a single O vacancy at $CeO_2(111)$.Corresponding structures are presented in Figure S2.

Figure S2	а	b	с	d	e	f
E_{ν}/eV	2.42	2.28	2.25	2.21	2.07	1.94

The oxygen vacancy formation energy (E_v) was calculated as follows:

$$E_{\nu} = \frac{1}{N} \Big(E_{CeO_{2-\delta}} + \frac{N}{2} E_{O_2} - E_{CeO_2} \Big),$$

where N is the number of oxygen atoms removed from the clean $\text{CeO}_2(111)$. $E_{CeO_2-\delta}$, E_{O_2} , and E_{CeO_2} represent the DFT total energies of reduced $\text{CeO}_2(111)$, gas-phase oxygen molecule and clean $\text{CeO}_2(111)$, respectively.



Fig. S2 Optimized structures of $CeO_2(111)$ with one (a-c) top- or (d-f) sub-surface O vacancy. Ce^{3+} ions are in deep blue.

Table S2 Calculated average formation energies of three O vacancies at $CeO_2(111)$.

Figure S3	а	b	с	d	e	f
E_{ν}/eV	2.89	2.72	2.45	2.34	2.31	2.30

Corresponding structures are in Figure S3.



Fig. S3 Optimized structures of CeO₂(111) with three O vacancies.



Fig. S4 Ce^{3+} distributions before and after H adsorption at stoichiometric $CeO_2(111)$, 1OV and 3OV. Ce^{3+} ions are in deep blue.



Fig. S5 Calculated structures of different surface states within the H_2 and H_2O formation processes at three different surfaces.

	Stoichiometric CeO ₂ (111)		10V		30V	
	Before H	After H	Before H	After H	Before H	After H
	adsorption	adsorption	adsorption	adsorption	adsorption	adsorption
Ce-1	9.6567	9.6463	9.6704	9.6976	10.0248	10.0285
Ce-2	9.6519	9.8546	9.8640	9.8741	9.6906	9.9542
Ce-3	9.6566	9.6476	9.6751	9.9193	9.9280	9.9571

Table S3 Bader charges (before and after the H adsorption) of the three Ce atomswhich bond with the top-surface O that takes the H at three surfaces.

	Stoichiometric CeO ₂ (111)	10V	30V
H coupling barrier/eV	3.51	2.93	2.08
H ₂ O formation barrier/eV	1.44	1.45	1.48

 Table S4 Calculated energy barriers for surface reactions of H at three different surfaces.



Fig. S6 Calculated structures of stable states along the multi-step surface H diffusion.

Stoichiometric	Diffusion (each number represents the O layer that the H	Barrier/eV	
CeO ₂ (111)	adsorbs at)		
	$1 \rightarrow 1$ [Direct surface diffusion]	3.49	
	$1 \rightarrow 1$ (rotation)	1.15	
	$1 \rightarrow 2$ (transfer)	0.51	
	$2 \rightarrow 2$ (rotation) [Multi-step surface diffusion]	0.05	
	$2 \rightarrow 1$ (transfer)	0.10	
	$1 \rightarrow 1$ (inverse-rotation) ^a	0.11	
	$2 \rightarrow 2$ (rotation) [bulk diffusion]	0.01	
	$2 \rightarrow 3$ (transfer)	0.14	
	$3 \rightarrow 3$ (rotation)	0.44	
	3→4 (transfer)	0.23	
	$4 \rightarrow 4$ (rotation)	0.14	
	$4 \rightarrow 5$ (transfer)	0.18	
10V	Diffusion (each number represents the O layer that the H	Barrier/eV	
	adsorbs at)		
	$1 \rightarrow 1$ (rotation)	1.07	
30 V	Diffusion (each number represents the O layer that the H	Barrier/eV	
	adsorbs at)		
	$1 \rightarrow 1$ (rotation)	0.84	

 Table S5 Calculated energy barriers for surface and bulk diffusions of H at three different surfaces.

^aStep 5 of Multi-step surface diffusion: OH rotates to point H toward the vacuum.

O-H bond energy

O-H bond energy of surface hydroxyl group can be obtained by rewriting the adsorption energy equation of H:

$$\begin{split} E_{ad}(H) &= E_{CeO_{x}} + \frac{1}{2}E_{H_{2}} - E_{H/CeO_{x}} = \left(E_{CeO_{x}} + \frac{1}{2}E_{H_{2}}\right) - \left(E_{CeO_{x}}^{'} + \frac{1}{2}E_{H_{2}} - E_{b}\right) \\ &= E_{CeO_{x}} - E_{CeO_{x}}^{'} + E_{b} = -E_{d} + E_{b} \\ &\Rightarrow E_{b} = E_{ad}(H) + E_{d}, \end{split}$$

where E'_{CeO_x} is the single point energy of H-CeO_x systems with the H atom being removed, E_b is the bond energy of O-H bond, and E_d is the deformation energy substituting for $E'_{CeO_x} - E_{CeO_x}$.