

## Electronic supplementary information

### Mechanistic study of the ceria supported, Re-catalyzed deoxydehydration of vicinal OH groups

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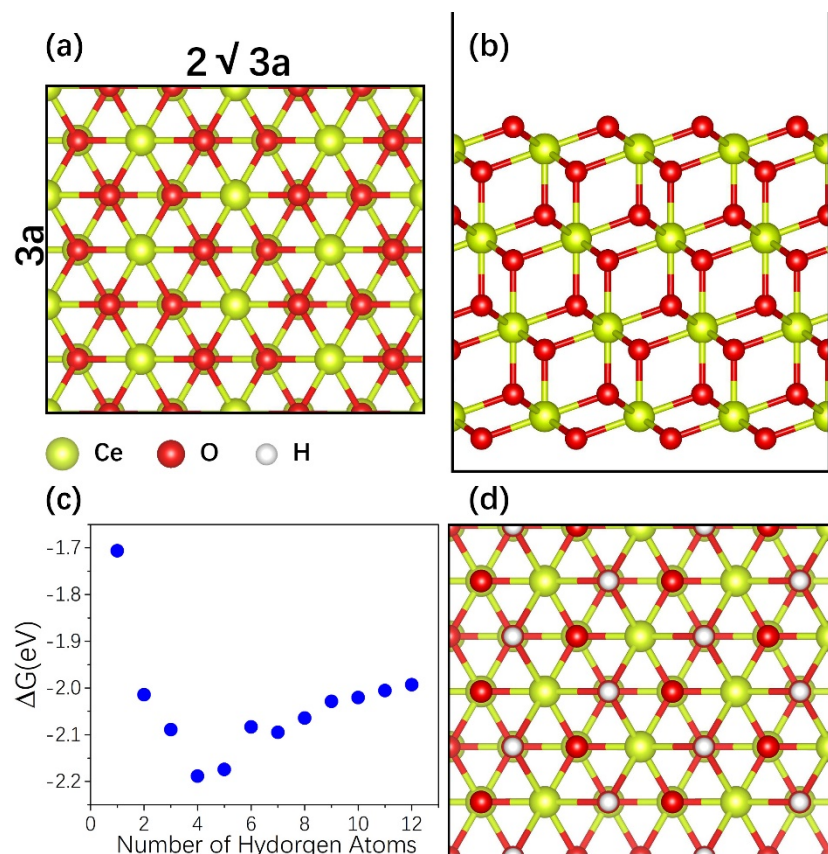
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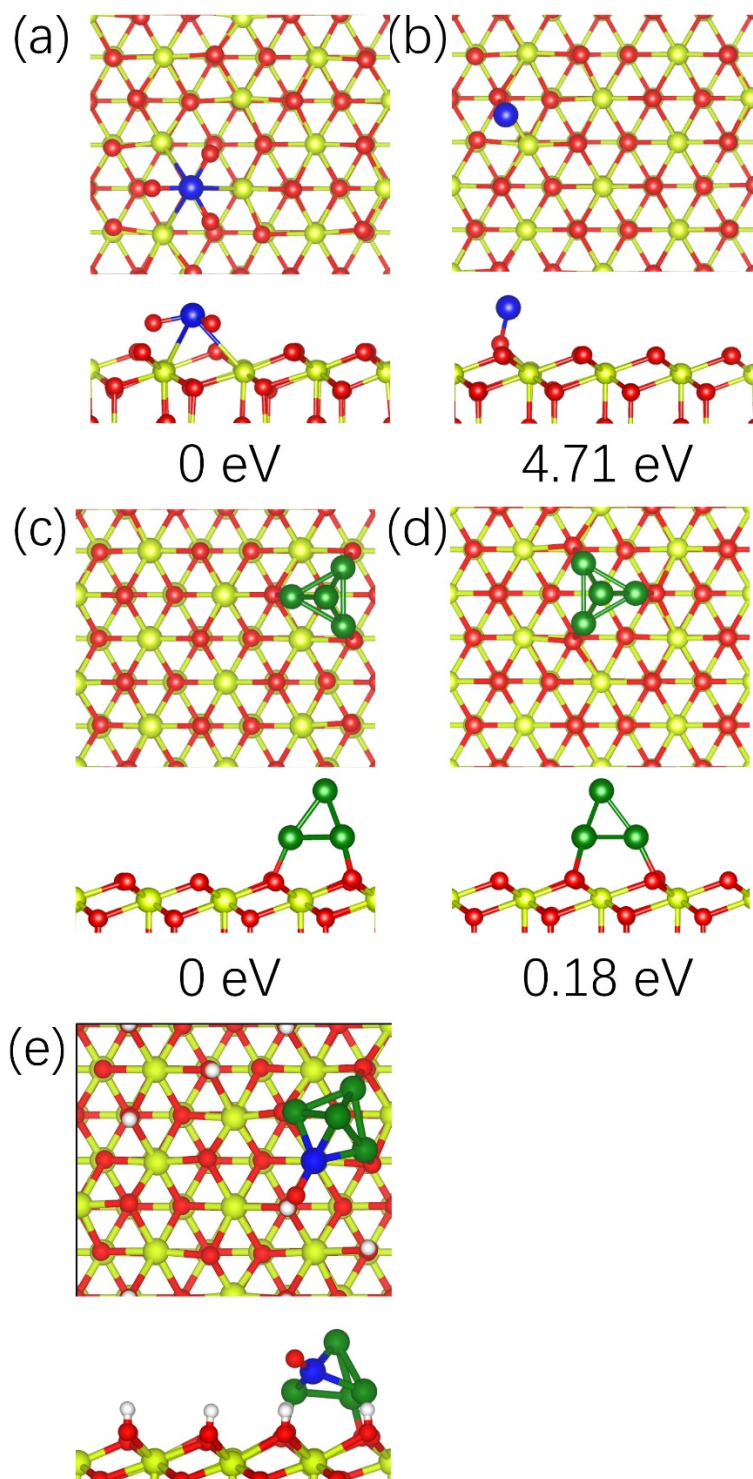
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## S1. Slab Model

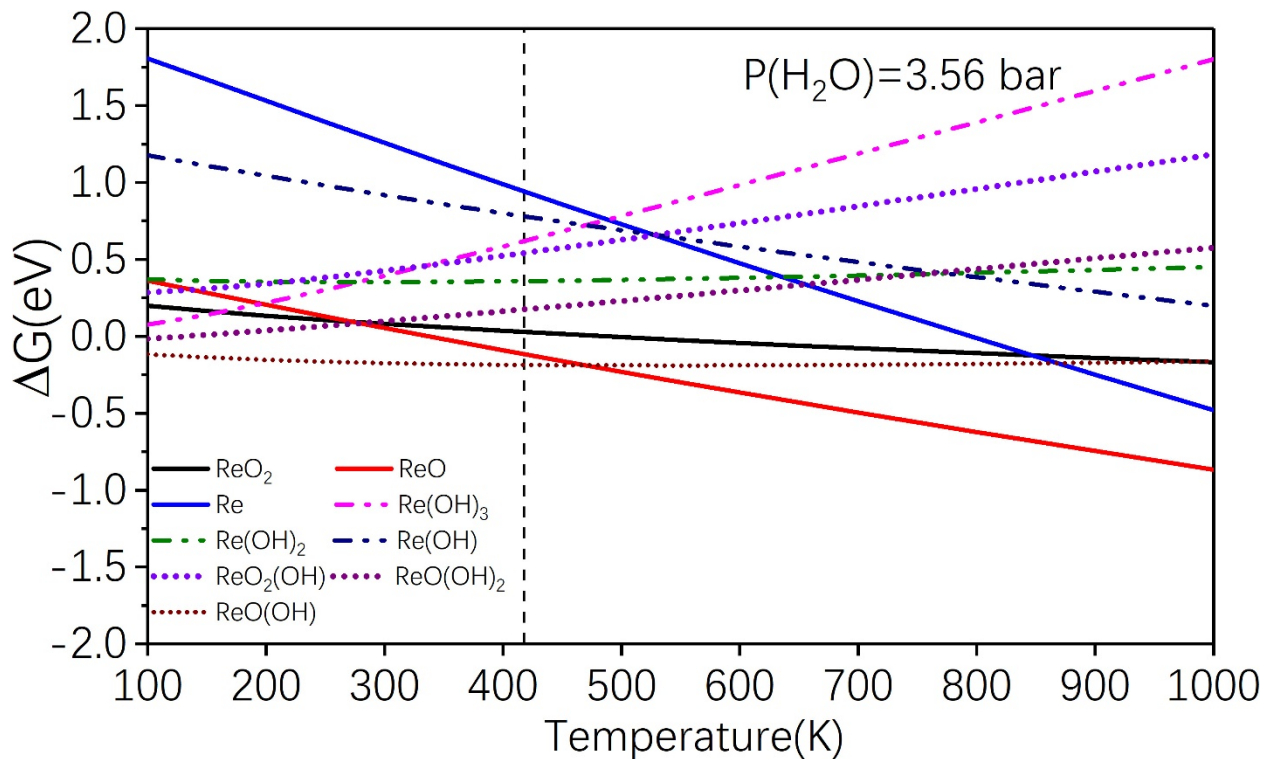


**Figure S1.** a. Top view of the  $(3 \times 2\sqrt{3})$   $\text{CeO}_2(111)$  surface model.  $a$  equals to  $3.871 \text{ \AA}$ , which is the optimized lattice constant of  $\text{CeO}_2$ . The topmost layer has 12 oxygen atoms; b. Side view of the  $\text{CeO}_2(111)$  surface model; c. Gibbs free energy of hydrogen adsorption on  $\text{CeO}_2(111)$  at 413 K, calculated as  $\Delta G = [G(\text{CeO}_2\text{H}_x) - G(\text{CeO}_2) - x/2 \cdot G(\text{H}_2)] / (x/2)$ ,  $x$  is the number of hydrogen atoms; d. Top view of the fully hydroxylated  $\text{CeO}_2$ , e.g.  $\text{CeO}_2\text{-H}_{12}$ .



**Figure S2.** Adsorption configuration and relative energies of Re (**a** and **b**) and Pd<sub>4</sub> (**c** and **d**) on CeO<sub>2</sub>(111). In the initial configurations, Re and Pd<sub>4</sub> of **a** and **c** are placed on top of a surface ceria O, while Re and Pd<sub>4</sub> of **b** and **d** are placed on top of a surface Ce. **e.** Adsorption configuration of ReO on Pd<sub>4</sub>.

## S2. Gibbs free energies of $\text{ReO}_x(\text{OH})_y$ species relative to $\text{ReO}_3$



**Figure S3.** The Gibbs free energies of  $\text{ReO}_x(\text{OH})_y$  species relative to  $\text{ReO}_3$  at a hydrogen partial pressure of 80 bar and a water partial pressure of 3.56 bar (corresponding to the chemical potential of liquid water at 413 K), respectively.

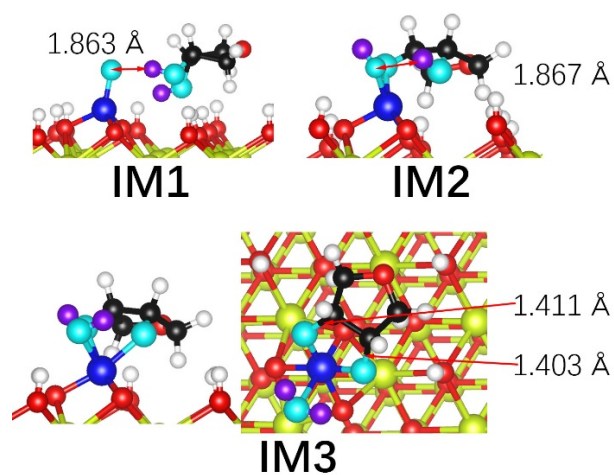
### S3. Partial pressure estimation of anhydroerythritol and dihydrofuran

In the experiments, 1 g of anhydroerythritol and 4 g of 1,4-dioxane solvent were used. This ratio was adopted in our calculation of the partial pressure (fugacity) of anhydroerythritol (AE) and dihydrofuran (DHF). We used the modified Raoult's law to calculate the partial pressure/fugacity of anhydroerythritol,

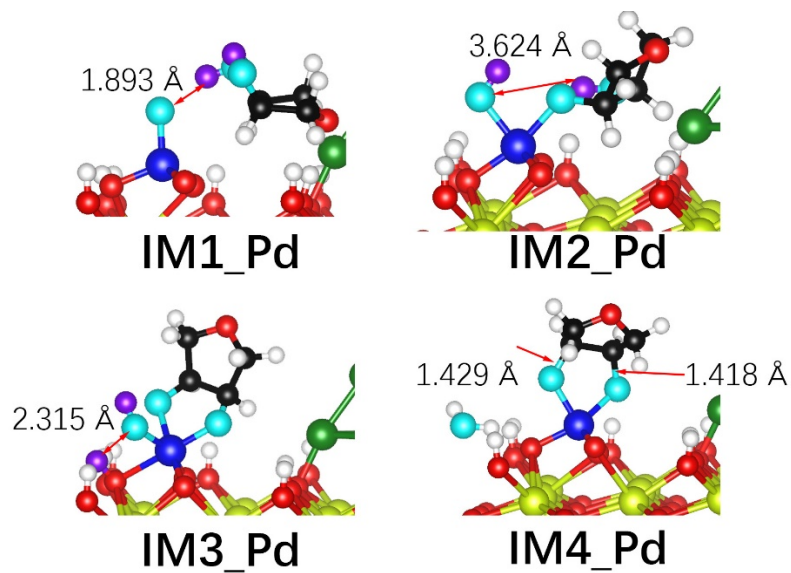
$$f_{AE} = P_{AE} = x_{AE} \times \gamma_{AE} \times P_{AE}^{sat}$$

where  $f_{AE}$ ,  $P_{AE}$ ,  $x_{AE}$ ,  $\gamma_{AE}$  and  $P_{AE}^{sat}$  denote fugacity, partial pressure, mole fraction, activity coefficient and saturation pressure of AE. The activity coefficient and saturation pressure of AE at 413 K were calculated with COSMOtherm,<sup>1</sup> being 2.79 and  $6.03 \times 10^{-3}$  bar, respectively. The mole fraction of AE in 1,4-dioxane is 0.175, therefore, the partial pressure of AE is  $2.95 \times 10^{-3}$  bar. The activity coefficient and the saturation pressure of DHF were calculated to be 2.77 and 4.98 bar, respectively. With the mole fraction of AE in 1,4-dioxane and the experimental conversion of AE to DHF (0.4), the partial pressure of DHF was estimated to be 0.965 bar. While the partial pressure of DHF might be overestimated at the initial stage of the reaction, we found that the reaction rate is essentially independent with the partial pressure/fugacity of DHF.

## S4. Labelling of selected lengths



**Figure S4.** The structures of IM1-IM3 in Figure 5 with selected length labelled.



**Figure S5.** The structures of IM1\_Pd-IM4\_Pd in Figure 7 with selected length labelled.

## S5. Formulation of harmonic transition state theory

Harmonic transition state theory was used to calculate elementary surface rate constants,  $k_f$  (forward rate) and  $k_b$  (backward rate)

$$k_f = \frac{k_B T}{h} e^{-\Delta G^{TS}/k_B T} \quad (1),$$

where  $k_B$  is the Boltzmann constant,  $T$  is the reaction temperature,  $h$  is the Planck constant, and  $\Delta G^{TS} = G^{TS} - G^r$  is the free energy of activation.  $k_b$  was calculated with  $\Delta G^{TS} = G^{TS} - G^p$ , where  $\Delta G^{TS}$  is the activation energy of the backward reaction.

Free energies of each species were calculated as

$$G = E_{DFT} + E_{ZPE} - k_B T \ln q_{vib} \quad (2).$$

Here,  $E_{DFT}$  and  $E_{ZPE} = \frac{1}{2} \sum_i h \nu_i$  are the DFT energy and zero point energy (ZPE), respectively.  $q_{vib}$  is the vibrational partition function. Each vibrational mode is labelled by  $i$ .

The vibrational partition function was calculated as

$$q_{vib} = \prod_i \frac{1}{1 - e^{-\frac{h \nu_i}{k_B T}}} \quad (3).$$

To reduce the error of small vibrational frequencies, we shifted all frequencies below  $100 \text{ cm}^{-1}$  to  $100 \text{ cm}^{-1}$ .<sup>2-3</sup> The free energies of reaction,  $\Delta G_{rxn}$ , are calculated in a similar way to  $\Delta G^{TS}$ . Thus, the equilibrium constant  $K_{eq}$  can be obtained as the ratio of forward and reverse rate constant.

The forward rate constant of an adsorption process was calculated using collision theory,

$$k_f = \frac{10^5}{\sqrt{2\pi m_A k_B T}} S_{unit} (s^{-1} atm^{-1}) \quad (4).$$

Here,  $m_A$  is the molecular weight of adsorbed species A,  $S_{unit}$  is the adsorption area of the active site which we approximated to be  $2.18 \times 10^{-19} \text{ m}^2$  in the present study. The desorption rate constant is obtained from the equilibrium constant, adsorption rate constant, and the relation  $K_{eq} = k_f/k_b$ .

The Gibbs free energies of the gas molecules were calculated using

$$G_{gas} = E_{DFT} + E_{ZPE} + \Delta \mu(T, P^\ominus) + k_B T \ln(P/P^\ominus) \quad (5),$$

where  $\Delta \mu$  can be calculated from the rotational, translational, and vibrational partition functions of the gas molecules, while  $P$  and  $P^\ominus$  represent the pressure of the gas molecule and 1 atm, respectively. The free

energies of the gas molecules were used to calculate the free energy of adsorption. The calculated rate constants of elementary steps for ReO/CeO<sub>2</sub> and ReO-Pd/CeO<sub>2</sub> are tabulated in Table S1 and Table S2.



## S6. Rate constants and free energies of all elementary steps

**Table S1.** Forward ( $k_f$ ) and backward ( $k_b$ ) reaction rate constant, free energy of activation ( $\Delta G^\ddagger$ ) and reaction free energy ( $\Delta G_{\text{rxn}}$ ) of each elementary step over ReO/CeO<sub>2</sub> at experimental conditions (413 K, 80 bar hydrogen pressure, etc.). For adsorption/desorption steps, only  $\Delta G_{\text{rxn}}$  are provided. R1→R14 and R19→R21 represent **Path-a** and **Path-b**, respectively. R1→R6, followed by R15→R18 which represents **Path-c**. The initial state (IS) and the final state (FS) are the same species, although they are represented differently in the elementary steps for clarity. NA denotes not-applicable. The matrix for solving the master equation is provided in supplementary datasheet, where  $f(n)$  and  $b(n)$  denote the forward and backward rate constant of  $n^{\text{th}}$  elementary step.

Reaction label	Elementary Steps	$k_f(\text{s}^{-1})$	$k_b(\text{s}^{-1})$	$\Delta G^\ddagger(\text{eV})$	$\Delta G_{\text{rxn}}(\text{eV})$
R1	AE(g)+IS→IM1	$8.165 \times 10^5$	$3.615 \times 10^{11}$	NA	0.46
R2	IM1→IM2	$1.440 \times 10^4$	$2.531 \times 10^6$	0.72	0.18
R3	IM2→IM3	$8.606 \times 10^{12}$	$1.775 \times 10^6$	0	-0.55
R4	IM3→IM4+H <sub>2</sub> O(g)	$4.049 \times 10^9$	$5.326 \times 10^7$	NA	-0.15
R5	IM4→IM5	$2.407 \times 10^{12}$	$1.480 \times 10^{-6}$	0.045	-1.49
R6	IM5→IM6+DHF(g)	$8.606 \times 10^{12}$	$3.980 \times 10^5$	NA	-1.15
R7	IM6→IM7	$6.282 \times 10^7$	$3.482 \times 10^7$	0.42	0.02
R8	IM7→IM10	$6.143 \times 10^{-25}$	$2.798 \times 10^{-24}$	3.04	0.05
R9	IM10→IM11	$3.627 \times 10^3$	$1.807 \times 10^{12}$	0.77	0.71
R10	IM11→IM12+H <sub>2</sub> O(g)	$1.557 \times 10^3$	$5.326 \times 10^7$	NA	0.37
R11	IM7+H <sub>2</sub> O(g)→IM8	$5.326 \times 10^7$	$8.606 \times 10^{12}$	NA	0.50
R12	IM8→IM9	$4.450 \times 10^{10}$	$8.606 \times 10^{12}$	0.19	0.19
R13	IM11→IM12+H <sub>2</sub> O(g)	$8.606 \times 10^{12}$	$5.326 \times 10^7$	NA	0.63
R14	IM12+H <sub>2</sub> (g)→IM13	$1.592 \times 10^{11}$	$8.606 \times 10^{12}$	NA	0.29
R15	IM13→FS	$1.153 \times 10^3$	$2.047 \times 10^{-18}$	0.81	-1.70
R16	IM7+1/2H <sub>2</sub> →IM16	$4.450 \times 10^{10}$	$1.573 \times 10^8$	0.19	-0.20
R17	IM16→IM17	$2.352 \times 10^{10}$	$8.606 \times 10^{12}$	0.21	0.21
R18	IM17→IM18+H <sub>2</sub> O(g)	$1.983 \times 10^7$	$5.326 \times 10^7$	NA	0.04
R19	IM18+1/2H <sub>2</sub> →FS	$4.450 \times 10^{10}$	$5.975 \times 10^6$	0.19	-0.32
R20	IM6+H <sub>2</sub> →IM14	$1.592 \times 10^{11}$	$4.692 \times 10^6$	NA	-0.37
R21	IM14→IM15	$2.532 \times 10^{-10}$	$2.057 \times 10^{-7}$	1.85	0.24
R22	IM15→FS+H <sub>2</sub> O(g)	$4.932 \times 10^9$	$5.326 \times 10^7$	NA	-0.16

**Table S2.** Forward ( $k_f$ ) and backward ( $k_b$ ) reaction rate constant, free energy of activation ( $\Delta G^\ddagger$ ) and reaction free energy ( $\Delta G_{\text{rxn}}$ ) of each elementary step over ReO-Pd/CeO<sub>2</sub> at experimental conditions (413 K, 80 bar hydrogen pressure, etc.). R1→R15, R16→R23, R24-R27 and R28-R30 represent **Path-d, f, g** and **e**, respectively. The matrix for solving the master equation is provided in supplementary datasheet, where  $f(n)$  and  $b(n)$  denote the forward and backward rate constant of  $n^{\text{th}}$  elementary step.

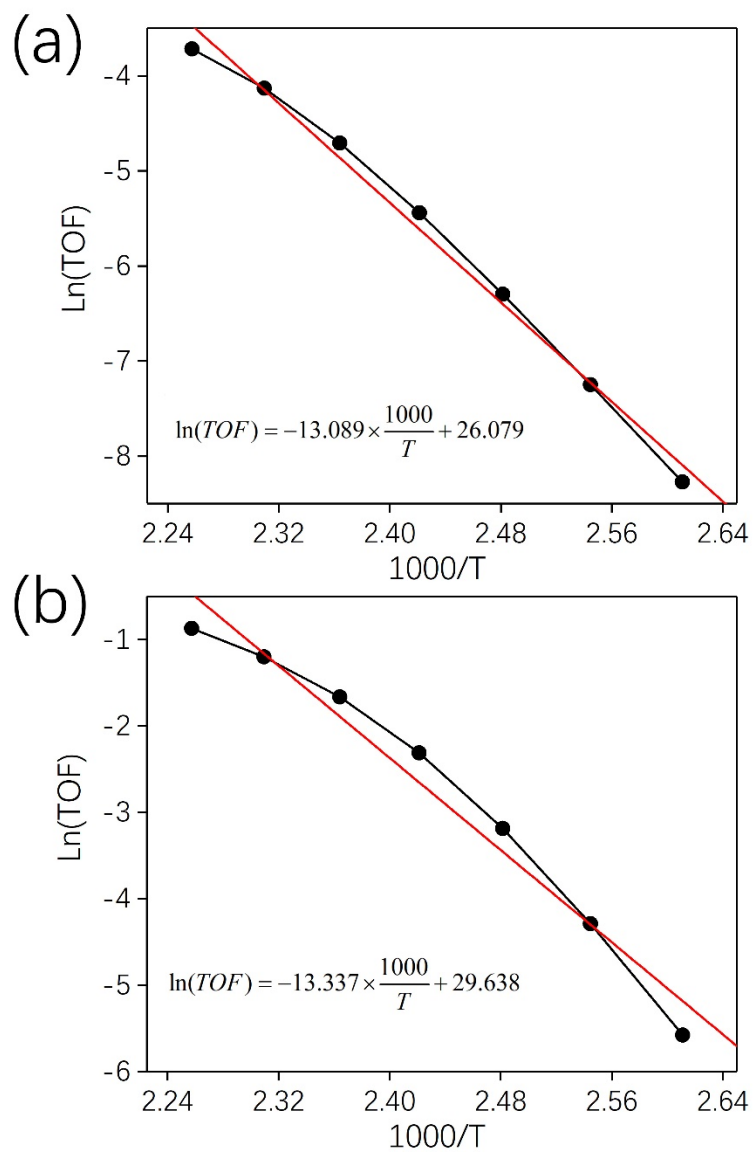
	Elementary Steps	$k_f(\text{s}^{-1})$	$k_b(\text{s}^{-1})$	$\Delta G^\ddagger(\text{eV})$	$\Delta G_{\text{rxn}}(\text{eV})$
R1	AE(g)+IS_Pd→IM1_Pd	8.165x10 <sup>5</sup>	5.078x10 <sup>9</sup>	NA	0.31
R2	IM1_Pd→IM2_Pd	1.116x10 <sup>8</sup>	8.606x10 <sup>12</sup>	0.40	0.40
R3	IM2_Pd→IM3_Pd	1.239x10 <sup>9</sup>	4.631x10 <sup>2</sup>	0.31	-0.53
R4	IM3_Pd→IM4_Pd	2.083x10 <sup>11</sup>	1.296x10 <sup>9</sup>	0.13	-0.18
R5	IM4_Pd→IM5_Pd +H <sub>2</sub> O(g)	1.055x10 <sup>7</sup>	5.326x10 <sup>7</sup>	NA	0.06
R6	IM5_Pd→IM6_Pd	1.205	3.204x10 <sup>2</sup>	1.05	0.20
R7	IM6_Pd→IM7_Pd +DHF(g)	8.606x10 <sup>7</sup>	3.980x10 <sup>5</sup>	NA	-0.66
R8	IM7_Pd→IM8_Pd	1.036x10 <sup>8</sup>	7.150x10 <sup>12</sup>	0.40	0.40
R9	IM8_Pd +H <sub>2</sub> O(g)→IM9_Pd	5.326x10 <sup>7</sup>	2.037x10 <sup>6</sup>	NA	-0.12
R10	IM9_Pd→IM10_Pd	2.282x10 <sup>10</sup>	8.606x10 <sup>12</sup>	0.21	0.21
R11	IM10_Pd→IM11_Pd +H <sub>2</sub> O(g)	1.238x10 <sup>7</sup>	5.326x10 <sup>7</sup>	NA	0.05
R12	IM11_Pd→IM12_Pd	5.747x10 <sup>3</sup>	2.275x10 <sup>10</sup>	0.75	0.54
R13	IM12_Pd→IM13_Pd +H <sub>2</sub> O(g)	9.633x10 <sup>10</sup>	5.326x10 <sup>7</sup>	NA	-0.27
R14	IM13_Pd +H <sub>2</sub> (g)→IM14_Pd	1.592x10 <sup>11</sup>	8.606x10 <sup>12</sup>	NA	0.22
R15	IM14_Pd→FS_Pd	7.496x10 <sup>8</sup>	7.114x10 <sup>-18</sup>	0.33	-2.13
R16	IM13_Pd +H <sub>2</sub> (g)→IM17_Pd	1.592x10 <sup>11</sup>	9.915x10 <sup>8</sup>	NA	-0.18
R17	IM17_Pd +H <sub>2</sub> O(g)→IM18_Pd	5.326x10 <sup>7</sup>	1.586x10 <sup>6</sup>	NA	-0.13
R18	IM18_Pd→IM19_Pd	1.419x10 <sup>11</sup>	2.274x10 <sup>-2</sup>	0.15	-1.05
R19	IM19_Pd→IM20_Pd	8.606x10 <sup>12</sup>	3.391x10 <sup>12</sup>	0.00	-0.03
R20	IM20_Pd→IM21_Pd	3.098x10 <sup>12</sup>	8.606x10 <sup>12</sup>	0.04	0.04
R21	IM21_Pd→IM22_Pd	8.606x10 <sup>12</sup>	3.645x10 <sup>12</sup>	0.00	-0.03
R22	IM22_Pd→IM23_Pd	8.606x10 <sup>12</sup>	2.957x10 <sup>10</sup>	0.00	-0.20
R23	IM23_Pd→FS_Pd +H <sub>2</sub> O(g)	5.326x10 <sup>7</sup>	4.643x10 <sup>3</sup>	NA	-0.33
R24	IM8_Pd +1/2H <sub>2</sub> →IM24_Pd	2.282x10 <sup>10</sup>	7.311x10 <sup>-1</sup>	0.21	-0.86
R25	IM24_Pd→IM25_Pd +H <sub>2</sub> O(g)	1.317x10 <sup>9</sup>	8.606x10 <sup>12</sup>	0.31	0.31
R26	IM25_Pd→IM26_Pd	1.266x10 <sup>8</sup>	5.326x10 <sup>7</sup>	0	-0.03
R27	IM26_Pd +1/2H <sub>2</sub> (g)→FS_Pd	2.282x10 <sup>10</sup>	1.454x10 <sup>-1</sup>	0.21	-0.92
R28	IM7_Pd +H <sub>2</sub> (g)→IM15_Pd	1.592x10 <sup>11</sup>	8.606x10 <sup>12</sup>	NA	0.18
R29	IM15_Pd→IM16_Pd	4.142x10 <sup>-5</sup>	2.986x10 <sup>-12</sup>	1.42	-0.59
R30	IM16_Pd→FS_Pd +H <sub>2</sub> O(g)	8.606x10 <sup>12</sup>	5.326x10 <sup>7</sup>	NA	-0.70

## S7. Chemical formulas of reaction intermediates

**Table S3.** Chemical formulas of reaction intermediates on ReO/CeO<sub>2</sub> and ReO-Pd/CeO<sub>2</sub>. In all cases, the ceria substrate with a formula of Ce<sub>48</sub>O<sub>96</sub> is omitted for brevity. The oxidation states of Re are also provided.

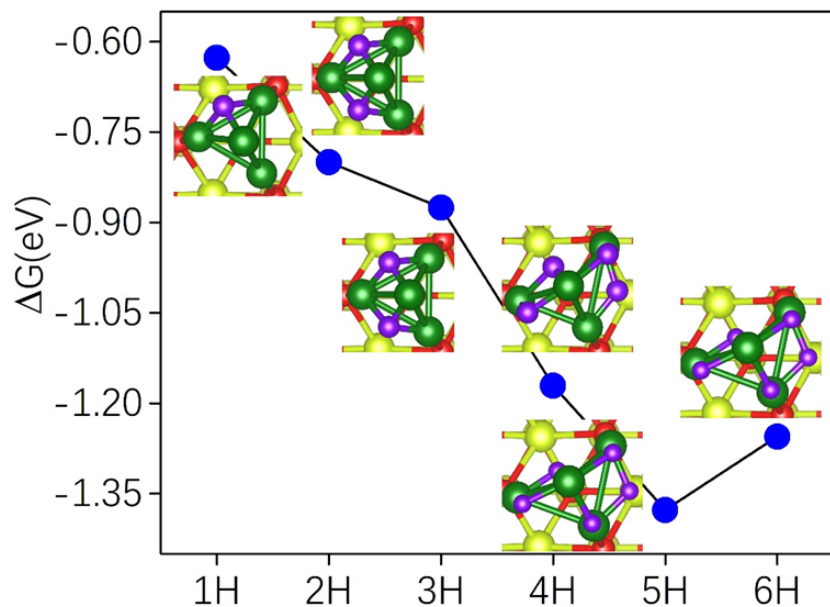
ReO/CeO <sub>2</sub>			ReO-Pd/CeO <sub>2</sub>		
Reaction intermidate	Chemical Formula	OS of Re	Reaction intermidate	Chemical Formula	OS of Re
IS/FS	H <sub>9</sub> ORe	6	IS_Pd/FS_Pd	H <sub>6</sub> OPd <sub>4</sub> Re	7
IM1	C <sub>4</sub> H <sub>17</sub> O <sub>4</sub> Re	6	IM1_Pd	C <sub>4</sub> H <sub>14</sub> O <sub>4</sub> Pd <sub>4</sub> Re	7
IM2	C <sub>4</sub> H <sub>17</sub> O <sub>4</sub> Re	5	IM2_Pd	C <sub>4</sub> H <sub>14</sub> O <sub>4</sub> Pd <sub>4</sub> Re	6
IM3	C <sub>4</sub> H <sub>17</sub> O <sub>4</sub> Re	5	IM3_Pd	C <sub>4</sub> H <sub>14</sub> O <sub>4</sub> Pd <sub>4</sub> Re	6
IM4	C <sub>4</sub> H <sub>15</sub> O <sub>3</sub> Re	5	IM4_Pd	C <sub>4</sub> H <sub>14</sub> O <sub>4</sub> Pd <sub>4</sub> Re	6
IM5	C <sub>4</sub> H <sub>15</sub> O <sub>3</sub> Re	7	IM5_Pd	C <sub>4</sub> H <sub>12</sub> O <sub>3</sub> Pd <sub>4</sub> Re	6
IM6	H <sub>9</sub> O <sub>2</sub> Re	7	IM6_Pd	C <sub>4</sub> H <sub>12</sub> O <sub>3</sub> Pd <sub>4</sub> Re	7
IM7	H <sub>9</sub> O <sub>2</sub> Re	7	IM7_Pd	H <sub>6</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
IM8	H <sub>11</sub> O <sub>3</sub> Re	7	IM8_Pd	H <sub>6</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
IM9	H <sub>11</sub> O <sub>3</sub> Re	7	IM9_Pd	H <sub>8</sub> O <sub>3</sub> Pd <sub>4</sub> Re	7
IM10	H <sub>9</sub> O <sub>2</sub> Re	7	IM10_Pd	H <sub>8</sub> O <sub>3</sub> Pd <sub>4</sub> Re	7
IM11	H <sub>9</sub> O <sub>2</sub> Re	7	IM11_Pd	H <sub>6</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
IM12	H <sub>7</sub> O <sub>1</sub> Re	7	IM12_Pd	H <sub>6</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
IM13	H <sub>9</sub> ORe	7	IM13_Pd	H <sub>4</sub> O <sub>1</sub> Pd <sub>4</sub> Re	7
IM14	H <sub>11</sub> O <sub>2</sub> Re	7	IM14_Pd	H <sub>6</sub> O <sub>1</sub> Pd <sub>4</sub> Re	7
IM15	H <sub>11</sub> O <sub>2</sub> Re	6	IM15_Pd	H <sub>8</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
IM16	H <sub>10</sub> O <sub>2</sub> Re	6	IM16_Pd	H <sub>8</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
IM17	H <sub>10</sub> O <sub>2</sub> Re	6	IM17_Pd	H <sub>6</sub> O <sub>1</sub> Pd <sub>4</sub> Re	7
IM18	H <sub>8</sub> O <sub>1</sub> Re	6	IM18_Pd	H <sub>8</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
			IM19_Pd	H <sub>8</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
			IM20_Pd	H <sub>8</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
			IM21_Pd	H <sub>8</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
			IM22_Pd	H <sub>8</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
			IM23_Pd	H <sub>8</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
			IM24_Pd	H <sub>7</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
			IM25_Pd	H <sub>7</sub> O <sub>2</sub> Pd <sub>4</sub> Re	7
			IM26_Pd	H <sub>5</sub> O <sub>1</sub> Pd <sub>4</sub> Re	7

## S8. Apparent activation energies



**Figure S6.** Arrhenius plot for **Path-c** (a) and the overall process of **Path-d, e, f** and **g** (b) in the temperature range 383–443 K.

### S9. Effect of pre-adsorbed hydrogen on the property of Re.

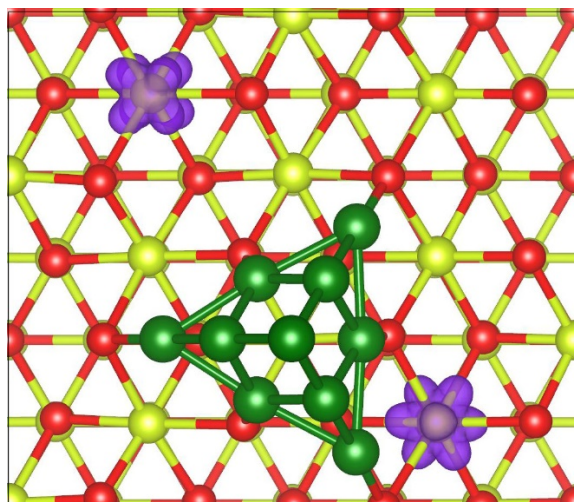


**Figure S7.** Adsorption free energies of hydrogen on CeO<sub>2</sub>-supported Pd<sub>4</sub> cluster, calculated as  $\Delta G = G(\text{PdH}_x) - G(\text{Pd}_4) - x/2 [G(\text{H}_2)]$ ,  $x$  is the number of hydrogen atoms. The adsorption energies suggest that Pd<sub>4</sub> can accommodate up to 5 hydrogen atoms.

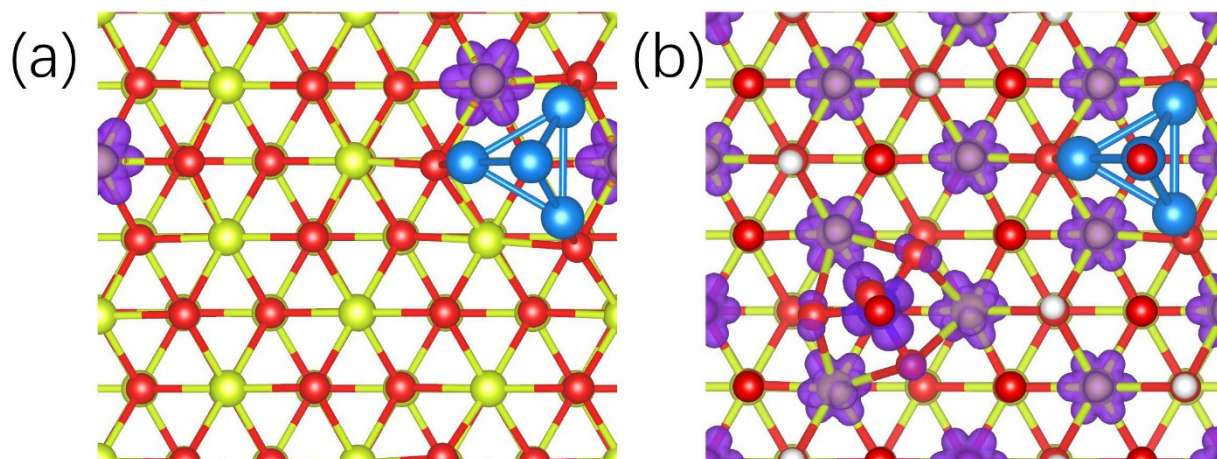
**Table S4.** Bader charge and d-orbital magnetic moment ( $\mu_B$ ) of Re for ReO species. Free energies  $G$  (in eV) of ReO<sub>2</sub> and ReOOH species relative to ReO under various hydrogen coverages are also provided. These values suggest that upon the adsorption of hydrogen on Pd<sub>4</sub>, the properties of Re are essentially unchanged.

	Pd <sub>4</sub> no-H	Pd <sub>4</sub> 3H	Pd <sub>4</sub> 4H	Pd <sub>4</sub> 5H
Bader(Re)	2.378	2.363	2.368	2.505
d-electron magnetic moment ( $\mu_B$ ) of Re	0.165	0.167	0.131	0.014
$G(\text{ReO}_2)$	1.10	0.97	0.86	1.09
$G(\text{ReOOH})$	0.64	0.46	0.41	0.38

## S10. Effect of the size of Pd cluster and Au<sub>4</sub> on the property of Re.



**Figure S8.** Spin density of ReO and Pd<sub>10</sub> adsorbed on pristine CeO<sub>2</sub>(111).



**Figure S9.** (a) Spin density of Au<sub>4</sub> adsorbed on pristine CeO<sub>2</sub>(111); (b) Au<sub>4</sub> and ReO co-adsorbed on a surface hydroxylated CeO<sub>2</sub>(111). Gold atoms in blue.

### Reference

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