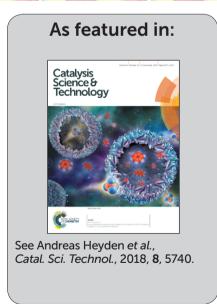


Highlighting research from Dr Andreas Heyden *et al.* from the Chemical Engineering Department, University of South Carolina, Colombia, United States

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Mechanistic study of the ceria supported, recatalyzed deoxydehydration of vicinal OH groups†

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Deoxydehydration (DODH) is an emerging biomass deoxygenation process whereby vicinal OH groups are removed. Based on DFT calculations and microkinetic modeling, we seek to understand the mechanism of the Re-catalyzed deoxydehydration supported on CeO₂(111). In addition, we aim at understanding the promotional effect of Pd in a heterogeneous ReO_v-Pd/CeO₂ DODH catalyst system. We disentangle the contribution of the oxide support, the oxide-supported single ReO_x species, and a co-adsorbed Pd promoter that has no direct interaction with the Re species. In the absence of a nearby Pd cluster, a Re site is able to reduce subsurface Ce-ions of a hydroxylated CeO₂(111) surface, leading to a catalytically active Re +6 species. The effect of Pd is twofold: (i) Pd catalyzes the hydrogen dissociation and spillover onto CeO2, which is an indispensable process for the regeneration of the Re catalyst, and (ii) Pd adsorbed in close proximity to Re on CeO₂(111) facilitates the oxidation of Re to a +7 oxidation state, which leads to an even more active Re species than the Re +6 site present in the absence of Pd. The latter promotional effect of Pd (and change in oxidation state of Re) disappears with increasing Pd-Re distance and in the presence of oxygen defects on the ceria support. Under these conditions, the ReO_x-Pd/CeO₂ catalyst system exhibits appreciable activity consistent with recent experiments. The established mechanism and role of various species in the catalyst system help to better understand the deoxydehydration catalysis. Also, the importance of the Re oxidation state and the identified oxidation state modification mechanisms suggest a new pathway for tuning the properties of metal-oxide supported catalysts.

1. Introduction

Utilization of biomass by transforming it into fuels and chemicals is a promising approach for achieving global sustainability. Compared to fossil resources, biomass-derived raw materials are usually oxygen-rich, necessitating the reduction of the oxygen content to valorize biomass. Various deoxygenation systems have been developed to convert biomass to value-added chemicals, such as dehydration, hydro-

deoxygenation,4 decarbonylation,5 and decarboxylation.6 In the quest for improved deoxygenation catalysts, there is a flurry of interest in the deoxydehydration process, which is the removal of two vicinal OH groups, converting a vicinal diol to an alkene. In Cook and Andrew's seminal work of DODH in 1996, they reported a homogeneous Re catalyst with PPh3 as the reductant to regenerate the catalyst.8 As a commercial organometallic compound, methyltrioxorhenium (MTO), has been extensively explored as a model DODH catalyst. 9,10 Later, V (ref. 11) and Mo-based12 homogeneous DODH catalysts were also developed as replacements for the high cost rhenium compounds. The first heterogeneous DODH catalyst, ReOx supported on activated carbon, was reported in 2013, albeit with leaching of catalyst into the solvent and fast activity loss. 13 Most of the subsequently reported heterogeneous DODH catalysts were also based on Re, supported on ceria¹⁴ or titania.¹⁵ Very recently, a non-Rhenium DODH catalyst, MoO_x/TiO₂ was reported. 16 Commonly held perceptions on the mechanism of a DODH process involve the following steps: (1) breaking of the two diol OHbonds by the catalyst and forming a diolate species and an adsorbed H₂O. The water molecule can usually desorb readily. This is also called the condensation step. (2) The desorption of the alkene from the low valent catalyst, leaving an additional

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 $[\]dagger$ Electronic supplementary information (ESI) available: Slab Model, Gibbs free energies of $\text{ReO}_x(\text{OH})_y$ species relative to ReO_3 at high water partial pressure, partial pressure estimation of anhydroerythritol and dihydrofuran, labelling of selected bond lengths, formulation of harmonic transition state theory, energetics, free energies, and rate constants of all elementary steps, apparent activation energy calculations, the effect of pre-adsorbed hydrogen on the properties of Re, atomic coordinates of all intermediate and transition states along reaction pathways (in VASP format). Matrices for solving the master equations is provided as supplementary datasheet. See DOI: 10.1039/c8cy01782d

oxygen on the catalyst and forming a high valent species, known as the extrusion step. (3) The regeneration of the catalyst by a reductant, that is the reduction step. PPh_3 , 8Na_2SO_3 , 17 and alcohols 18 are commonly used reductants in the DODH reaction. Efforts have also been made for using more practical reductants such as H_2 (ref. 9) and CO. 19

Recently, Tomishige et al. reported a CeO2 supported ReOx DODH catalyst for which the Re species are atomically dispersed.14,20 Through screening of various oxide supported Re catalysts, they found that CeO2 is the best support of Re while the presence of the co-adsorbed palladium can promote the activity and selectivity of the catalyst significantly. Using H₂ as reductant, a ReO_x-Pd/CeO₂ (Re = 2 wt%, Pd/Re = 0.25) catalyst exhibited a remarkable selectivity for the conversion of cis-1,4anhydroerythritol (AE) to dihydrofuran (DHF), which is further hydrogenated to tetrahydrofuran (THF). The active site was proposed to be monomeric Re species stabilized on the CeO₂ support. The turnover frequency (TOF) per Re atom at 443 K was calculated to be $\sim 0.083 \text{ s}^{-1}$, one order of magnitude larger than typical of homogeneous catalysts at the same temperature.²⁰ While not all Re species are monomeric, it has been proposed that only isolated Re species are catalytically active. It has also been estimated that about 90% of the Re did not interact with Pd and that the Pd-bound Re species are inactive. The coordination number of Pd-Pd is about 3, implying that Pd species are highly dispersed.¹⁴

As a common practice to improve the catalytic performance, a small concentration of impurity elements are added to a catalyst, known as promoter.²¹ For example, potassium is used as a promoter for ammonia synthesis²² and Fischer–Tropsch synthesis.²³ While literature reports of promotional phenomena in catalysis are abundant, detailed mechanistic insights have been rare.^{24–28} Concerning the ReO_x–Pd/CeO₂ DODH catalyst, it is intriguing to understand the behavior of the Pd promoter. In particular, how does the co-adsorbed Pd modifies the properties of the monomeric Re without forming chemical bonds with Re remains an open question.

In the present study, we determine the energy profile of various reaction pathways and unravel the promotional effect of Pd using density functional theory (DFT). Through ab initio thermodynamics calculations, we determined the structure of the monomeric Re species. Following the experimental condition, we also used AE as a substrate molecule to examine the catalytic DODH reaction on ReOx/CeO2, which was compared with that of ReOx-Pd/CeO2. Since the DHF hydrogenation to form THF is a fast step and well-understood, we did not include this step in our investigation. Next, we developed a microkinetic model (MKM) to gain further insights into the reaction mechanism. A novel pathway of ReOx reduction by H₂ is proposed that is distinct from those on homogeneous catalysts. To our knowledge, this is the first systematic study of the mechanism of the heterogeneous DODH reaction. Considering that Ce has localized 4f orbitals, it is possible to count²⁹ the electron transfer from the adsorbed species to the CeO2 support and to assign the oxidation state of the supported species. Based on the analysis of the Re oxidation

state, we propose an oxidation state modification mechanism: the presence of Pd can change the oxidation state of nearby Re via the CeO₂ substrate. We finally extend the discussion to the effect of oxygen vacancies in the ceria support, Pd cluster size, and other noble metal clusters like Au.

2. Methods

2.1 First principles methods

First-principles calculations were performed using periodic density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP 5.4.1).30,31 The spinpolarized generalized gradient approximation (GGA) with the PBE functional was used to treat exchange-correlation effects. A plane wave basis set with a cutoff energy of 500 eV was selected to describe the valence electrons. The electronion interactions were described by the projector augmented wave (PAW)^{32,33} method. The Brillouin zone integration was performed with a $2 \times 2 \times 1$ Monkhorst-Pack³⁴ (MP) k-mesh and Gaussian smearing ($\sigma = 0.05$ eV). An effective Hubbard U value of 5.0 eV was used to describe the strong on-site Coulomb repulsion of the Ce 4f electrons, following previous research.35 To confirm our DFT+U results, we performed for selected species calculations with the Heyd, Scuseria, and Ernzerhof (HSE06) hybrid functional.³⁶ We used Grimme's DFT-D3 (ref. 37) scheme to include the van der Waals interactions semi-empirically. The SCF and force convergence criteria for structural optimization were set to 1×10^{-6} eV and 0.01 eV Å⁻¹, respectively. The climbing image nudged elastic band (CI-NEB)38 and dimer methods39,40 were used to optimize the transition state structures. The optimized conventional cell of ceria with a lattice parameter of 3.871 Å was adopted to construct the oxygen terminated 41 CeO2(111) surface. A $(3 \times 2\sqrt{3})$ supercell with four O-Ce-O trilayers and 15 Å vacuum slab (Fig. S1a and b†) was used to describe the ceria support during the catalytic process. Solvation effects are not explicitly considered in our calculations due to difficulties in modeling solvation effects for processes at solidliquid interfaces. 42 Fortunately, the DODH reaction has been found to occur most favorably in 1,4-dioxane which is a nonpolar solvent that displays often only a minor influence on a catalyst's activity, 43,44 justifying our approach of initially neglecting direct solvent effects.

2.2 Microkinetic model

Harmonic transition state theory was used to calculate all elementary rate constants of surface processes. Collision theory with a sticking coefficient of 1 was used to estimate the rate constants for adsorption processes. While the sticking coefficient may not be 1 in liquid phase reactions, the overall kinetics is hardly affected by the choice of sticking coefficient since the adsorption steps are not rate-controlling but in quasiequilibrium (*vide infra*). Details of the formulation is provided in the ESI.† We used typical experimental reaction conditions in our models. The partial pressures (chemical potentials) of

AE and DHF were estimated using COSMOtherm⁴⁵ (ESI†). A H₂ partial pressure of 80 bar was used. The experiments were performed with water solvent, as well as non-water solvent such as 1,4-dioxane. The latter is the optimal experimental condition and is also used to investigate the reaction pathways in the present study. Nonetheless, the presence of water is unavoidable under 1,4-dioxane solvent conditions since small amounts of water are commonly found in gas (hydrogen) streams and since the DODH reaction itself produces water. We approximate the water partial pressure for reactions in 1,4-dioxane solvent as being 0.1% of the H₂ pressure, i.e., 0.08 bar (low water partial pressure scenario). We use the equilibrium water vapor pressure at 413 K, i.e., 3.56 bar, for reactions in liquid water (high water partial pressure scenario). The calculated rate constants are tabulated in Tables S1 and S2.† After obtaining the rate constants of each elementary step, we developed a Master equation of probability densities for the system to occupy each discrete state and solved for the steady-state solution. Here, the probability densities are also referred to as surface coverage θ . We solved the Master equation using the BzzMath46 library. The reaction rate (turnover frequency) of each pathway was calculated using the obtained surface coverages. The apparent activation energy $(E_{\rm app})$ was calculated from the overall rates over a temperature range of 383-443 K using the expression

$$E_{\rm app} = RT^2 \left(\frac{\partial \ln r}{\partial T} \right)_{P, y_i} \tag{1}$$

where the total pressure (P) and the mole fraction of species i in the reaction mixtures (y_i) were kept constant.

The reaction order (α_i) with respect to species i at a specific temperature (T) is calculated by varying the partial pressure of the species (P_i) using the relation

$$\alpha_{i} = \left(\frac{\partial \ln r}{\partial \ln P_{i}}\right)_{T, P_{j+i}} \tag{2}$$

To identify rate controlling steps and states in the microkinetic models, we also perform a Campbell's degree of kinetic (KRC) and thermodynamic (TRC)^{47,48} rate control analysis.

$$KRC_{i} = \left(\frac{\partial \ln r}{\partial \ln k_{i}}\right)_{K_{i},k_{i}\neq k_{i}}$$
(3)

where K_i is the equilibrium constant of step i.

$$TRC_{n} = \left(\frac{\partial \ln r}{\partial \left(-\frac{G_{n}}{k_{B}T}\right)}\right)_{G = G^{TS}}$$
(4)

where G_n is the free energy of adsorbate n and G_i^{TS} is the free energy of the transition state i, respectively.

2.3 Construction of atomistic models

Based on the $(3 \times 2\sqrt{3})$ CeO₂(111) surface model, we built the atomistic models for ReOx-Pd/CeO2 and ReOx-Pd/CeO2 catalysts by unravelling the structure of the ReO_r species. The hydrogen pressure in Tomishige's study was high, which can be indicative of the formation of hydroxyls on ceria under reaction conditions. 49 Indeed, our calculations suggest that the adsorption of hydrogen on ceria is favorable with an exergonicity of -1.99 eV per H2 at full hydrogen coverage (Fig. S1c†). The high exergonicity of hydrogen adsorption can be attributed to the large electron affinity of ceria caused by the low-lying 4f states of Ce4+.50 As such, we adopt the fully-hydrogenated CeO2(111) surface to construct a model of the DODH catalyst. Next, we examined the interaction of Re with ceria. We found that a Re atom can bind with three oxygen atoms on the pristine CeO₂(111) surface either above a surface O or a surface Ce atom (Fig. S2a and b†). The former configuration is 4.71 eV more stable than the later and was adopted for subsequent calculations. To model the atomically dispersed Re species on ceria under reaction condition, we first replaced three H atoms (released as 3/2 H₂) from the fully-hydrogenated CeO₂(111) with one Re, which is exergonic by 4.5 eV. The CeO₂(111) supported Re can accommodate some amount of oxygen atoms, forming Re oxide. In the presence of H2, the Re oxide can also be hydrogenated to $ReO_x(OH)_y$. We found that x + ycan be in the range of 0 to 3; additional O or OH lead to the detachment of ReO_x(OH)_v from the CeO₂(111) surface. The optimized structures of various CeO2 supported ReO_x(OH)_v species are displayed in Fig. 1a. We evaluated the thermodynamic stability of ReO_x(OH)_v species at a fixed pressure of H₂ and H₂O, with the temperature varying from 100 to 1000 K. The relative stability of ReO_x(OH), in the low water partial pressure case, corresponding to favorable experimental conditions, is presented in Fig. 1b. ReO is found to be the energetically most stable species at 413 K while ReO(OH) and ReO2 are 0.07 eV and 0.29 eV higher in energy than ReO, respectively, despite the fact that ReO(OH) is the most stable form of isolated Re sites on ceria at 413 K in our high water partial pressure scenario (Fig. S3†). The free energies of other species are well above these three species at 413 K. In the ensuing investigation, we focused our attention on the low water partial pressure scenario and the model of the ReO/CeO2 catalyst (model-A) is shown in Fig. 2a and c. The model of the ReO-Pd/CeO2 catalyst (model-B, Fig. 2b and d) is constructed by replacing 3 H atoms with a Pd₄ cluster in tetrahedral conformation, adsorbed on its most stable adsorption site on the ceria surfaced (model-A, Fig. S2c and d†). Here, any direct interaction between Re and Pd is avoided. The replacement of 3 H atoms with Pd4 is exergonic by 2.21 eV. Here, we also examined an adsorption configuration of a ReO species on a Pd4 cluster (Fig. S2e†) rather than the ReO species and the Pd4 cluster being separated as is the case in model-B. Due to the oxophilic nature of Re, the Pd4-loaded ReO is 2.13 eV

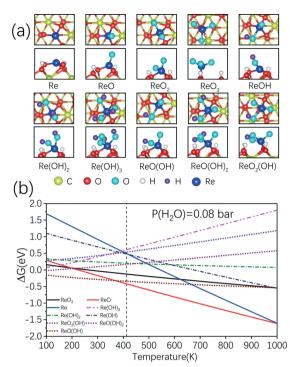


Fig. 1 a. Optimized structures of various $ReO_x(OH)_y$ species adsorbed on hydroxylated CeO_2 . b. The Gibbs free energies of $ReO_x(OH)_y$ species relative to ReO_3 with a hydrogen partial pressure of 80 bar and water partial pressure of 0.08 bar, respectively. The free energy of $ReO_x(OH)_y$ relative to ReO_3 is balanced by adding H_2 and H_2O_y , e.g. $\Delta G(ReO_2) = G(ReO_3) + G(H_2) - G(ReO_2) - G(H_2O)$.

higher in energy than model-B. Next, we verified the relative stability of ReO, ReO(OH), and ReO₂ at 413 K for ReO_x-Pd/CeO₂, concluding that Re-O remains the most stable species in the presence of Pd, with ReO(OH) and ReO₂ being 0.64 and 1.10 eV higher in energy, respectively. Therefore, the adoption of model-B as the atomistic model ReO-Pd/CeO₂ is justified.

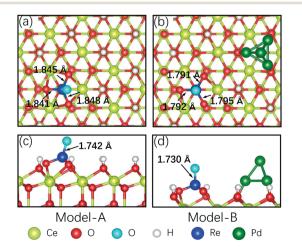


Fig. 2 Top view (a) and side view (c) for the model of ReO/CeO_2 (model-A); top view (b) and side view (d) for the model of $ReO-Pd/CeO_2$ (model-B). Re-O bond lengths are labeled.

3. Results

3.1 Proposed reaction pathway

Having established an atomistic model of ReO/CeO2 and ReO-Pd/CeO₂ catalysts, we performed a mechanistic study of AE deoxydehydration over the two catalysts. As mentioned, an additional oxygen will be left on the catalyst after the DODH reaction. In the present case, ReO will be converted to ReO2, making it necessary to regenerate the catalyst by reducing the ReO₂ with hydrogen. In principle ReO₂ can be directly reduced by H2, yet the activation energy can be high (vide infra), inconsistent with the high catalytic activity of ReO-Pd/ CeO2. Therefore, we proposed an alternative pathway for ReO2 reduction by the hydrogen of the hydroxyls on ceria displayed in Fig. 3, which is also applicable in model-B where a co-adsorbed Pd cluster is included. Steps I and II correspond to the aforementioned condensation step of the DODH. Step III is the desorption of the alkene (the facile desorption of water is also included). In step IV, a hydrogen atom (Ha) migrates to a neighboring oxygen bonded to Re, creating a hydrogen vacancy (H_{vac}) on the hydroxylated CeO₂. Next, another hydrogen (Hb) replenishes the vacancy created by the removal of H_a (step V), which is followed by the formation of water (step VI). The catalytic cycle is closed when H₂O desorbs (VII) and the two hydrogen vacancies are replenished by dissociative adsorption of H₂ (step VIII).

3.2 DODH reaction of AE over ReO/CeO₂

We computed the free energy profiles of the DODH reaction of AE over ReO/CeO₂ along with the surface hydrogen migration pathways, as displayed in Fig. 4a. We report all energy barriers in free energy scale while the DFT energy profiles are also provided as a reference. The associated structures of initial/final states and intermediate states are presented in Fig. 5 and S4 and Table S2.† We found that an AE molecule adsorbs weakly on ReO/CeO2, which is endergonic by 0.47 eV (path-a). In the adsorbed state (IM1), one hydrogen of the hydroxyl group of AE binds through a hydrogen bond with the protruding oxygen of ReO. This hydrogen then forms a chemical bond with the Re oxygen, concomitant with formation of another Re-O bond. The first O-H bond-breaking forms IM2 which involves overcoming a free energy barrier of 0.72 eV (all reported activation energies are on a free energy scale unless stated otherwise). The breaking of the second O-H is accompanied with the formation of H₂O and a Re-O bond. This step was found to be barrierless, which can be attributed to the close vicinity of the AE hydrogen with the Re-bonded OH and thus, the strong tendency to form a H₂O in IM3. The formed H₂O can desorb readily, forming IM4. Next, C-O bond-breaking can occur readily with a free energy barrier of 0.05 eV(IM4 -> IM5), followed by the desorption of the physisorbed DHF (IM5 \rightarrow IM6). The formed ReO₂ state (IM6) is then allowed to be reduced by the hydroxyl-hydrogen on ceria. The steps of IM6 → IM7 and IM7 → IM10 correspond to the steps d and e in Fig. 3. Consistent with a previous computational study that hydrogen migration on CeO₂ has a

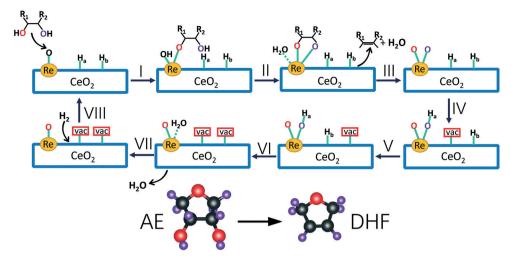


Fig. 3 Schematics of the deoxydehydration of vicinal diol over ceria supported Re-O, followed by catalyst regeneration through a surface hydrogen migration process. Reaction steps are labelled as I-VIII. Stable configurations of AE and DHF are presented. Here, carbon, oxygen, and hydrogen atoms are represented in black, red, and purple, respectively.

high barrier,⁵¹ the energy barrier of step IM7 → IM10 is 3.04 eV in our study. Owing to the insurmountable barrier of direct hydrogen migration, we also considered the waterassisted surface hydrogen migration, or a so-called Grotthus

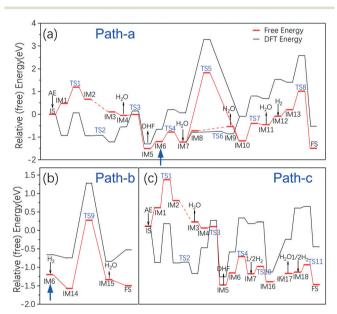


Fig. 4 Energy profiles of AE DODH reaction over ReO/CeO2 using model-A. a. Surface hydrogen migration mechanism with the hydrogen vacancies replenished by dissociation of H2. b. Direct reduction of ReO₂ by H₂. c. Surface hydrogen migration mechanism with atomic hydrogen assumed to be abundant, IS, IM and FS denote initial state, intermediate state and final state, respectively. Red dashed line denotes that the free energy barrier (T = 413 K and experimental partial pressures given in section 2) of an elementary step vanishes (e.g. $IM2 \rightarrow IM3$). For $IM16 \rightarrow IM17$, the DFT energy barrier vanishes. The intermediate state where the reaction paths bifurcates is indicated by a blue arrow. The free energy of activation and reaction free energy are also provided in Table S1.† A chemical formula description of all structures is given in Table S3.†

mechanism, which has a significantly reduced activation energy. 52,53 Indeed, we found that the free energy barrier of hydrogen migration in the presence of water (IM8 → IM9) vanishes and the activation energy was assigned to be the endergonicity of the forward reaction (0.19 eV). The ReO₂ reduction process is completed in IM10 → IM11. Then, the formed water desorbs readily, leaving two hydrogen vacancies on the hydroxylated ReO/CeO2 surface, which should be replenished in the ensuing steps. In the present case, however, the dissociation of H_2 on CeO_2 (IM13 \rightarrow FS) has a high energy barrier of 0.81 eV. For comparison, we also examined the direct reduction of ReO2 by hydrogen, which has an energy barrier of 1.85 eV (IM14 → IM15 in Fig. 4b, path-b). Considering the energy of TS8 relative to IM6 is 2.22 eV and is even larger than the energy barrier of IM14 → IM15, the surface hydrogen migration process has a higher effective barrier than the direct reduction process and the latter is mainly responsible for the reduction of ReO2. If the dissociation of H₂ is facile and the hydrogen vacancies can be replenished readily (e.g. through hydrogen spillover), another surface hydrogen migration process, whereby ReOOH species is involved; (Fig. 4c, path-c), is also made feasible. In this case, we also assume that the dissociation of H₂ is independent of the reactions occurring near ReO/ReO2 and that replenishment of one H_{vac} by 1/2 H₂ in IM7 has only an activation energy of the water-assisted hydrogen migration on CeO₂ (0.19 eV). The reaction then takes place between the Re-bonded OH and the hydrogen of the surface hydroxyl (IM16 → IM17), which is followed by the replenishment of the newly formed H_{vac} (IM18 \rightarrow FS). To this end, the catalytic cycle is also complete. The effective barrier of ReO₂ reduction along path-c is only 0.72 eV. Briefly, the reactions of path-a and b take place over pristine ReO/ReO2, for which the energy profiles are not favorable, while a more favorable path-c is feasible only when the replenishment of Hvac can readily occur (due to the presence of *e.g.* a Pd site close-by).

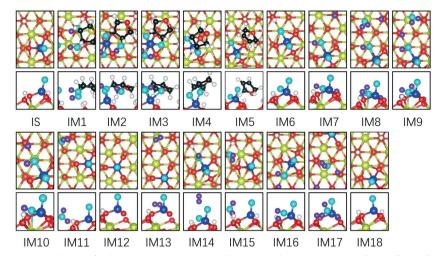


Fig. 5 The structures (top view and side view) of initial state and intermediate states for the energy profiles in Fig. 4. Black and purple balls denote carbon and hydrogen atoms, respectively. The other color patterns are the same as in Fig. 1. A chemical formula description of all structures is also given in Table S2.†

3.3 DODH reaction of AE over ReO-Pd/CeO₂

Consistent with experimental observations, our computational results suggest that the DODH of AE over ReO/CeO2 has a low activity. We next investigated the reaction over ReO-Pd/CeO2 with model-B and the energy profile is displayed in Fig. 6, corresponding to the surface hydrogen migration mechanism where the hydrogen vacancies are replenished by dissociation of H2 on a ceria site (path-d), ReO2 reduced directely by H₂ molecule (path-e), the hydrogen spillover from Pd cluster onto ceria and the replenishment of H vacancy (path-f) and H vacancy replenishment through surface hydrogen migration mechanism with atomic hydrogen assumed to be abundant (path-g). The associated structures of the initial, intermediate, and final states are presented in Fig. 7 and S5.† The scission of the first O-H bond for AE has a barrier of 0.40

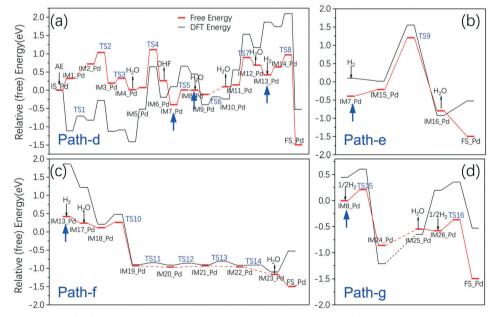


Fig. 6 (Free) energy profiles of AE DODH reaction over ReO-Pd/CeO₂ using model-B (T = 413 K and experimental partial pressures given in section 2). a. Surface hydrogen migration mechanism with the hydrogen vacancies replenished by dissociation of H2 on a ceria site. b. Direct reduction of ReO₂ by H₂. c. The two hydrogen vacancies of IM13_Pd replenished through hydrogen spillover from Pd₄ onto CeO₂ d. hydrogen vacancy of IM8_Pd replenished through surface hydrogen migration mechanism with atomic hydrogen assumed to be abundant (equivalent scenario to pathc but with the presence of a Pd cluster). The _Pd extension for all transition states are omitted for brevity. The intermediate states where the reaction paths bifurcate are indicated by blue arrows. The free energy of activation and reaction free energy are also provided in Table S2.† A chemical formula description of all structures is given in Table S3.†

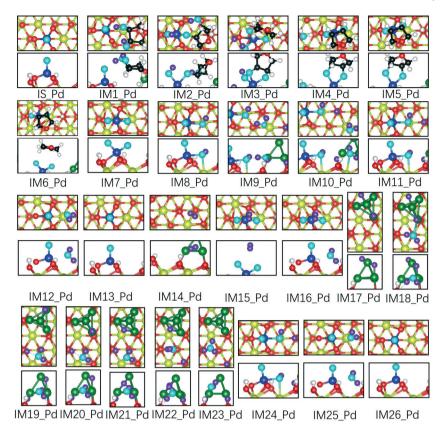


Fig. 7 The structures (top and side view) of initial state and intermediate states for the energy profiles in Fig. 6.

eV (IM1_Pd \rightarrow IM2_Pd), lower than that for ReO/CeO₂ (pathd). In the second O-H scission step (IM2_Pd → IM3_Pd), the hydrogen originally belonging to the Re-bonded OH migrates to an oxygen pertaining to the CeO2 substrate, while the Rebonded OH returns immediately after accepting the hydrogen from the second OH of AE, concomitant with the formation of a new Re-O bond. Subsequently, a H₂O molecule is formed, followed by the desorption of H₂O and DHF. The second O-H bond breaking of AE over ReO-Pd/CeO₂ has an effective barrier of 1.03 eV (TS2_Pd relative to IS_Pd), lower than the effective barrier of 1.18 eV for ReO/CeO2 (TS1 relative to IS in Fig. 4a), which is indicative of a more facile DODH over ReO- Pd/CeO_2 . The DHF formation step (IM5_Pd \rightarrow IM6_Pd) has a barrier of 1.05 eV and the effective barrier of TS4_Pd is 1.11 eV. As compared with the ReO/CeO2 counterpart, the high barrier can be explained by the fact that C-O bond breaking over ReO-Pd/CeO2 is endergonic by 0.20 eV while that of ReO/ CeO₂ is exergonic by 1.51 eV.

Similar to the reaction over ReO/CeO2, the reduction of the ReO₂ species for ReO-Pd/CeO₂ in IM7_Pd also involves a surface hydrogen migration process and subsequent replenishment of hydrogen vacancies. Here, only the waterfacilitated hydrogen migration was considered. TS7_Pd, corresponding to the transition state of the water formation by reducing ReO₂, is 1.29 eV above IM7_Pd in the free energy diagram. Physisorption of H2 on IM13 is endergonic by 0.22 eV and the dissociation of H_2 on ReO-Pd/CeO₂ (IM14_Pd \rightarrow

FS_Pd) has a barrier of 0.33 eV. The low barrier of H₂ dissociation is likely related to the interaction between the two hydrogen vacancies and the neighboring Pd4 cluster. Overall, the effective barrier of ReO2 reduction along path-d is 1.37 eV. The direct reduction of ReO2 by hydrogen for ReO-Pd/ CeO₂ (IM15_Pd → IM16_Pd in path-e, Fig. 6b) has a barrier of 1.42 eV. The reduced barrier, as compared with the ReO/ CeO₂ counterpart, can be attributed to the higher exergonicity of ReO₂ reduction for ReO-Pd/CeO₂ (-0.94 eV) than for the ReO/CeO₂ catalyst model (0.24 eV, IM14 → IM15 in path-b).

In the presence of a co-adsorbed Pd cluster, the replenishment of the two hydrogen vacancies can harness the facile dissociation of hydrogen on Pd.54 Hence, we considered the hydrogen spillover from Pd4 onto the CeO2 support (Fig. 6c, pathf). The dissociative adsorption of a H₂ molecule on Pd₄ is barrierless and IM13_Pd → IM17_Pd was treated as an adsorption process. In the hydrogen spillover process, a hydrogen migration on CeO2 is needed; therefore, we introduced a preadsorbed water that has been proven to facilitate hydrogen migration. The H₂O molecule is stabilized by Pd₄ (IM18_Pd). Due to the close vicinity of H and H₂O, the first hydrogen migration from Pd_4 to CeO_2 (IM18_Pd \rightarrow IM19_Pd) is passed on by water, following a Grotthus mechanism and replenishing a Hvac. Subsequently, the other hydrogen diffuses for two steps on the Pd₄ cluster to be in a favorable position for spillover onto CeO₂ (IM19_Pd \rightarrow IM20_Pd \rightarrow IM21_Pd). Then, the migration of

hydrogen to a second H_{vac} is assisted by water (IM21_Pd \rightarrow IM22_Pd) and the newly formed H_{vac} is replenished by hydrogen from the Pd₄ cluster (IM22_Pd \rightarrow IM23_Pd). Finally, the added water desorbs and the hydrogen spillover process is completed. The hydrogen spillover mechanism has very favorable kinetics, for which IM18_Pd \rightarrow IM19_Pd has a barrier of only 0.15 eV, while the other barriers vanish in the free energy scale. Comparing the energy profiles of path-d-f, we conclude that the hydrogen spillover mechanism is mainly responsible for the replenishment of hydrogen vacancies during the catalyst regeneration process.

Since the replenishment of hydrogen over ReO-Pd/CeO₂ is facile, it is reasonable to expect the reaction to occur following the surface hydrogen migration mechanism (path-g, Fig. 6d), with one $H_{\rm vac}$ replenished by "1/2 H_2 " and involvement of a ReO(OH) species (IM24_Pd, Fig. 7), which has an effective barrier of 0.41 eV. Path-c also becomes a possible process when a co-adsorbed Pd cluster on ceria is far away from the catalytic Re center, which does not alter the reactivity of the DODH, yet catalyzes the $H_{\rm vac}$ replenishment process.

3.4 Microkinetic modelling

Having established the energy profiles of each reaction, we developed MKMs for various reaction mechanisms for the DODH over the two catalysts and determined the degree of rate control under experimental reaction conditions. The MKM of the overall process for path-a and b suggests that its TOF at 413 K is 1.47×10^{-10} s⁻¹. The calculated vanishingly small TOF is qualitatively consistent with the experimental fact that the activity of the catalyst is low in the absence of any transition metal promoter. Although most of the Re exists in monomeric form in the prepared catalyst, there is some degree of agglomeration of a small portion of Re, which can contribute to a hydrogen spillover pathway and a TOF higher than the one calculated here. The KRC of TS9 approaches 1, suggesting that the kinetics of the DODH over Re/CeO₂ is controlled by the direct reduction of the ReO₂ species. When the reaction proceeds along path-c for which the replenishment of Hvac can readily occur, the TOF dramatically increases to $4.33 \times 10^{-3} \text{ s}^{-1}$. The reaction kinetics is controlled by TS1 whose KRC approaches 1. Here, the TRC of IM5 is -0.82, suggesting that destabilization of the DHF adsorbed state (IM5) leads to an increase in TOF. The overall TOF for path-d, g, e and f was found to be 9.90×10^{-2} s⁻¹. Unlike path-c, the kinetics for the overall process of path-d, g, e and f is primarily controlled by the C-O bond dissociation process (TS4_Pd) with a KRC of 0.93. In addition, the energy of the intermediate state IM4_Pd and the initial state IS_Pd have a significant effect on the reaction rate with TRC values of -1 and -0.44, respectively. The effective barrier of TS1 in path-c is 0.07 eV higher than TS4_Pd in path-d, which explains the lower activity (TOF) of path-c. As such, we can conclude that the roles of co-adsorbed Pd in ReO-Pd/CeO₂ are twofold: (a) Pd catalyzes the hydrogen spillover onto ceria, which enables the surface hydrogen migration process

through path-g and (b) Pd facilitates the breaking of AE O–H bonds on Re sites. However, it renders the C–O bond breaking more difficult than the absence of it. In other words, the effect of Pd is fully "turned on" for the reactions of path-d, g, e and f while it only behaves as a hydrogen spillover catalyst for path-c, representing two limiting cases.

The experimental TOF was reported at 443 K as 0.083 s⁻¹ (ref. 20) for ReO-Pd/CeO₂, while we obtained a higher TOF of 0.42 s⁻¹ under the same condition with our MKM. We note that the predicted TOF is for the DODH process while the experimentally measured value is for the consecutive process of DODH and the hydrogenation of DHF. Considering that the Pd-ceria interaction in the experiments is likely in-between the above-mentioned limiting cases and that underestimating the activation energy of the rate-determining step by only 1 kcal mol⁻¹ leads to a factor ~3 decrease in TOF, we consider the predicted TOF to be in very good agreement with the experimental value.

The apparent activation energies, E_{app} , of path-c, as well as the overall process of path-d-g were obtained within the temperature range of 383 to 443 K using an Arrhenius plot (Fig. S6†). The respective $E_{\rm app}$ were found to be 1.13 eV and 1.15 eV, respectively. Particularly for model-B (path-d-g), we observe a non-linear Arrhenius plot with a lower activation barrier at higher temperatures. The non-linearity can be explained by a decreasing importance of the product desorption process (C-O bond cleavages - TS4 Pd) with increasing temperature and a corresponding increase in importance of the initial O-H dissociation process (TS2_Pd). Specifically, the KRC of TS4_Pd decreases from 0.99 to 0.75 when increasing the temperature from 383 K to 443 K (i.e., the KRC of TS2_Pd increases from practically zero to 0.25). Considering that the energy barrier of the reaction involving TS2_Pd possesses a lower energy barrier than the one from TS4_Pd, the Arrhenius plot curves to lower values with increases temperature.

Next, the reaction order (α_i) with respect to H_2 was found to be 0, consistent with prior experimental results. With respect to the AE concentration, we found (consistent with the rate controlling steps for the models) a reaction order of 1 for model-A and 0.5 for model-B. Both reaction orders are somewhat consistent with prior experimental results that observed a decreasing AE reaction order with AE concentration. Finally, it should be mentioned that a water solvent is unfavorable for the DODH reaction, a MKM with a H2O pressure of 3.56 bar (water solvent condition) predicts for path-c an over one order of magnitude lower TOF $(1.12 \times 10^{-4} \text{ s}^{-1})$ as with a H_2O pressure of 0.08 bar $(4.33 \times 10^{-3} \text{ s}^{-1})$. The reduction in TOF can be understood by the higher stability of the ReO(OH) species relative to ReO at higher oxygen chemical potential in water (see Fig. S3†), reducing the number of active Re sites. For Path-d-g, the computed TOF at a H₂O pressure of 3.56 bar is $2.52 \times 10^{-3} \text{ s}^{-1}$ (versus $9.90 \times 10^{-2} \text{ s}^{-1}$ at low water chemical potential). The reduction in TOF can be explained by the free energy of TS4_Pd being increased by 0.13 eV relative to the initial state due to the change in H chemical potential.

3.5 Electronic interaction between CeO₂ and the supported species

So far, we have demonstrated a high catalytic activity of the ReO-Pd/CeO2 catalyst system for the DODH reaction. As their seems to be some medium-range communication between nearby (but not in direct contact) Pd and ReOx sites in the ReO-Pd/CeO₂ catalyst, we analyze the electronic interaction between CeO₂ and the supported species to provide insight into the promotional effect of Pd. Intuitively, ReO and the Pd₄ cluster tend to donate electrons to the f-orbital of Ce, reducing some Ce⁴⁺ to Ce³⁺. We employ the site-specific magnetic moment as a measure of the oxidation state (OS) of Re and Ce. The existence of Ce3+ is characterized by a f-electron magnetic moment of approximately 1 and the spin-density localized on Ce atoms (Fig. 8). The d-orbital magnetic moment, the Bader charge and the OS of Re, as well as the number of Ce³⁺ in our catalyst model are summarized in Table 1. It should be mentioned that the calculated magnetic moment of Re(vI) is ca. 0.6 μ_B which is less than 1 μ_B due to electron over-delocalization typical of DFT. For Re(vII), the d-orbital magnetic moment approaches 0. The difference in OS of different Re species is also confirmed by Bader charge analysis (see Table 1). The spin density of adsorbed ReO and Pd4 on both the pristine CeO₂(111) surface and the hydroxylated surface are visualized in Fig. 8. On pristine CeO₂(111), 5 Ce⁴⁺ were found to be reduced by the ReO species (Fig. 8a), for which Re reaches its highest oxidation state of +7. In contrast, there is essentially no charge transfer between the Pd₄ and CeO₂(111) (Fig. 8b). In the presence of both ReO and Pd₄ (Fig. 8c), 6 Ce-ions are reduced. On the OH-terminated/ hydroxylated CeO₂(111) surface, each H atom donates one electron to CeO₂(111), reducing the surface ceria atoms. Specifically, we found that 13 Ce4+ (all 12 surface Ce4+ and 1 subsurface Ce4+) are reduced for ReO on the hydroxylated ceria

Table 1 The d-electron magnetic moment (μ_B), the Bader charge and the OS of Re, as well as the number of reduced Ce-ions. (p) and (hy) denotes the prestine and hydroxylated ceria surface, respectively. H_v denotes a surface hydrogen "vacancy" on the hydroxylated ceria surface. Sub and top denote the position of the oxygen vacancy, i.e., if it is located in the subsurface or top layer, respectively

Species	Magnetic moment of Re	Bader charge of Re	OS of Re	Number of Ce ³⁺
ReO(p)	0.011	2.323	7	5
Pd(p)	NA	NA	NA	1
Pd-ReO(p)	0.031	2.368	7	6
ReO(hy)	0.577	2.187	6	13
ReO-1H _v (hy)	0.579	2.167	6	12
ReO-2H _v (hy)	0.135	2.414	$7 - \delta$	~ 12
$ReO-3H_v(hy)$	0.088	2.44	7	11
ReO(OH)(hy)	0.71	2.274	6	12
ReO ₂ (hy)	0.004	2.484	7	12
Pd(hy)	NA	NA	NA	10
Pd-ReO(hy)	0.165	2.372	$7 - \delta$	12
Pd-ReO(OH)(hy)	0.046	2.47	7	11
Pd-ReO ₂ (hy)	0.003	2.476	7	10
Pd-ReO ₂ (hy-double)	0.596	2.237	6	23
ReO(hy)-sub-OV	0.524	2.146	6	15
Pd-ReO(hy)-sub-OV	0.394	2.293	$6 + \delta$	13
ReO(hy)-top-OV	0.579	2.172	6	14
Pd-ReO(hy)-top-OV	0.508	2.233	6	12

surface (Fig. 8d). Considering the contribution of the 9 surface H atoms, the ReO species donates 4 electrons and the OS of Re is assigned to be +6. The d_{z^2} like spin density localized on the Re(vi) is illustrated in Fig. 8d. To confirm our DFT+U calculations, we also performed single-point calculations of ReO(hy) using the HSE06 functional. Again, we found a Re d-orbital magnetic moment of 0.65 $\mu_{\rm B}$ and 13 reduced Ce³⁺ ions. To understand the high OS of Re under the experimental reaction conditions (which are reducing), we realize that ceria can easily be reduced by adsorbed species such as Re that is stable in a +6 and +7 oxidation state but relatively

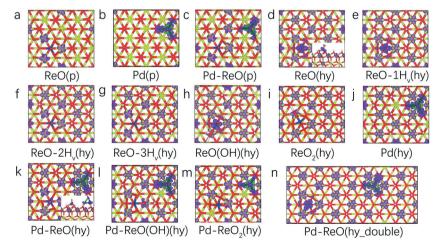


Fig. 8 Spin density of ReO and Pd adsorbed on pristine (p) CeO₂(111) (a-c) and surface hydroxylated (hy) CeO₂(111) (d-n). The insets of d and k show the side views. The spin density isosurfaces are set to 0.01 e Å $^{-3}$. There can be anti-parallel spin of neighboring Ce $^{3+}$ 4f electrons. Since we only consider the effect of charge transfer, the spin-ordering is not presented. It was found that energy difference between the ferromagnetical and antiferromagnetic states is less than 5 meV.56

unstable in a +5 OS. Also, the reduction of sub-surface Ce ions is more difficult than the reduction of surface Ce ions such that the Re species is only able to reduce one subsurface Ce ion.

To better understand the interaction between the reduced ceria support and the ReO species, we removed up to three H atoms from the ReO model supported on a hydroxylated ceria surface (Fig. 8e-g). In the case of one H vacancy, the number of electrons transferred to the Ce-ions is 12 (, i.e., all surface Ce-ions are reduced) and Re remains in a +6 state. Upon the removal of an additional H atom from the ceria surface, the electron affinity of the surface Ce-ions is strong enough to further oxidize Re. Note in Fig. 8f that the d-electron magnetic moment of Re is non-vanishing, therefore we assign a 7 – δ OS to Re (δ is a small positive number). Further removal of a third H atom (Fig. 8g) from the ceria surface leads to 11 Ce-ions being reduced, i.e., Re is in its highest possible oxidation state and it cannot donate any additional electrons to the ceria surface.

Next, we found that a Pd4 cluster adsorbed on a hydroxylated CeO₂ surface donates 1 electron (Fig. 8j), consistent with that on the pristine surface. When both ReO and a Pd4 cluster are coadsorbed on the hydroxylated CeO2 surface, the Pd4 cluster donates 1 electron and the ReO species donates 5 – δ electrons to the hydroxylated CeO2 surface, i.e., due to the presence of a nearby Pd4 cluster, the OS of Re is increased from +6 to ca. +7. To confirm this form of medium-range communication between the Re and Pd sites, we calculated the Re d-orbital magnetic moment with the HSE06 functional and found a magnetic moment of 0.31 μ_B , which is again significantly lower than the one in the absence of the Pd4 cluster. Pd-ReO(hy) core level shift⁵⁵ calculations suggest that the Re 4f level binding energy for Pd-ReO(hy) is 0.72 eV higher than that of the same catalyst model in the absence of the Pd cluster, corroborating the higher OS of the former case. The origin for the different OS of Re between ReO(hy) and Pd-ReO(hy) is that 3 surface H atoms can donate 3 electrons while Pd₄ only donates 1 electron to CeO₂ (i.e., the Pd cluster donates fewer electrons than the surface H atoms that would be present in the absence of the Pd cluster). Also the electron donation from ReO to CeO2 is "nonlocal" (i.e. not just the Ce3 triangle directly underneath ReO are reduced, which is seen in Fig. 8a). The nonlocal distribution of Ce3+ is consistent with previous studies which suggest that the two Ce3+ formed by removal of one oxygen on CeO₂(111) surface are situated at non-neighbouring positions. 56,57 Due to this nonlocality of electron donation, ReO tends to compensate the relatively poor electron-donation ability of the Pd cluster, leading to a high Re OS for Pd-ReO(hy). In this sense, the Pd cluster (even when not in direct contact with the Re-site) can be regarded as an oxidation state modifier of the Re-site via the CeO2 substrate. The assignment of the Re OS for other key intermediates including ReO(OH) (Fig. 8h and l) and ReO2 (Fig. 8i and m) on the reduced ceria surface along the reaction path, shown in Table 1, are all in agreement with the analysis above. To examine the interaction range between Re and Pd₄,

we created a $(3 \times 4\sqrt{3})$ hydroxylated surface with Re and Pd₄ placed at a more distant position than that of the $(2 \times 4\sqrt{3})$ surface (Fig. 8n). Here, the OS of Re is +6. Therefore, only one electron is transferred from the ReO region to the Pd4 region on CeO₂(111). It can be expected that a further increase of the distance between ReO and Pd4 leads to the absence of electron transfer, resembling the case of ReO(hy) (Fig. 8d). Overall, the extent to which Pd modifies the OS of Re is determined by their distance on CeO₂(111). The charge transfer process of CeO₂(111) supported Pd₄ and Re are schematically displayed on Fig. 9. In addition, the OS of Re for all reaction intermediates are provided in Table S3.†

The difference in Re OS influences the energetics of the intermediate states and the activity of the catalyst system. Specifically, the energies of ReO2 relative to ReO for the Pd4promoted system (IM7_Pd in path-d) and the non-promoted system (IM6 in path-a) are 1.10 eV and 0.29 eV, respectively. Also, the ReO(OH) species in path-g (IM24_Pd) is 0.64 eV higher in energy than ReO, while the counterpart of path-c (IM16) is only 0.07 eV higher. The different energies of the reaction intermediates are responsible for the above-mentioned different activity of path-c and the Pd-promoted case. Finally, we also considered the effect of adsorbed H on Pd4 on the properties of Re. Fig. S7 and Table S4 in the ESI† show that the properties of Re are only marginally changed in the presence of pre-adsorbed hydrogen on the Pd cluster.

Up to now, our computational study is based on an ideal scenario with a small Pd cluster loaded on a stoichiometric CeO₂(111) surface. It should be pointed out that the mechanism of the realistic DODH reaction catalyzed by ReO_x-Pd/

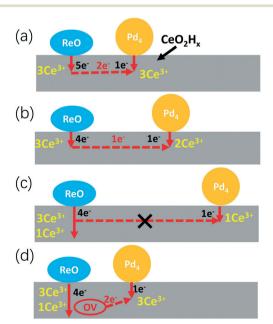


Fig. 9 Charge transfer process of ReO and Pd4 on a hydroxylated CeO₂(111) surface. a. Short distance, b. medium distance c. long distance between the ReO and Pd4 site. d. Effect of an oxygen vacancy on charge transfer (the case of Fig. 10b and f).

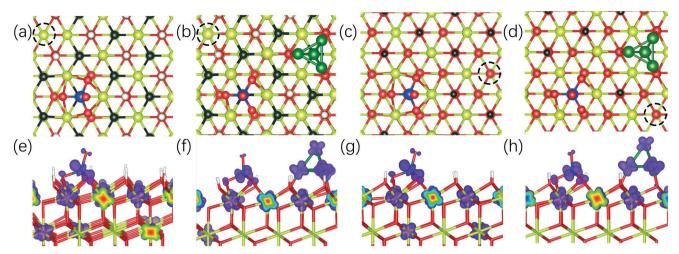


Fig. 10 ReO and Pd adsorbed on $CeO_2(111)$ with a subsurface oxygen vacancy (a and b) and surface oxygen vacancy (c and d). The subsurface oxygen is highlighted as a black ball and the position of the most stable oxygen vacancy site is indicated by a black circle (a and b). An OH group is removed to create a surface oxygen vacancy. The surface hydrogen is highlighted as black (c and d). The spin densities of e-h correspond to a-d, respectively.

CeO₂ is complicated by the presence of oxygen vacancies (OVs) on the ceria support, a size and facet effect of the CeO₂ support, and the surface coverage and ratio of ReO and Pd. We also mention here that the calculated OV formation free energy at 413 K and a H2 and H2O partial pressure of 80 and 0.08 bar, respectively, is calculated to be 1.62 eV. The most stable OV is stabilized at sub-surface position.⁵⁶ Despite the fact that we compute a highly endergonic OV free energy, surface and subsurface OVs have been observed experimentally in ceria.⁵⁶ We therefore examined the effect of both surface and subsurface OVs on the electronic properties of Re in the absence/presence of Pd4. Formation of a subsurface OV creates 2 Ce3+ while a surface OV creates 1 Ce3+ (since a OH group is removed to create the surface OV). Analysis of the spin densities (Fig. 10) suggests that in all cases Re has a +6 OS. The calculated magnetic moment and Bader charge of Re are presented in Table 1. A schematics of charge transfer process for the case of co-adsorbed Re and Pd4 in the presence of a sub-surface oxygen vacancy is displayed in Fig. 9d, corresponding to Fig. 10b and f. It appears that in the presence of oxygen vacancies even the Pd4-containing system leads to a Re OS of +6 (instead of +7 in the absence of defects). Hence, the promotional effect of Pd only manifests itself as a hydrogen spillover catalyst and the above-mentioned promotional effect of changing the oxidation state of Re vanishes. In a recent experimental study, the catalytic activity of a ReO_x-Pd/ CeO2 is not sensitive to the distance between Re and the Pd cluster.58 In other words, Pd only serves as H2 spillover catalyst and the modification of the electronic properties of Re is less pronounced. This might be related to the presence of oxygen vacancies in CeO2. To study the effect of Pd cluster size on the OS of Re, we repeated our oxidation state calculations for a Pd₁₀ cluster on a pristine CeO₂(111) surface (Fig. S8†). The Pd₁₀ cluster, which occupies 6 oxygen sites, donates 2 electrons to the CeO₂(111) support and for a model similar to

model-B, but with the Pd_4 cluster being replaced with Pd_{10} , the OS of Re is again +7. The overall effect of the adsorbed Pd metal cluster on the coadsorbed Re species is determined by the distance between Re and the Pd cluster, the presence of oxygen vacancies and only to a lesser extent the size of the metal cluster.

Recently, a Au promoted ReO_x/CeO₂ catalyst has also been found to catalyze the DODH reaction using H2 as reductant.58,59 To study how Au modifies the activity of a coadsorbed ReO active site, we replaced the Pd4 cluster with a Au₄ cluster in our catalyst model (see Fig. S9†). Oxidation state calculations suggest that Au, unlike Pd, interacts weaker with the ceria support and cannot modify the Re oxidation state, i.e., the Re exhibits a +6 OS. Consequently, the key role of the Au cocatalyst in the ReO_x-Au/CeO₂ catalyst system appears to be the H2 dissociation catalyzed by Au-ceria interface sites.60 Based on both the experimental and computational results, we conclude that the facile activation of H2 is a prerequisites for a DODH catalyst using H2 as reductant. Otherwise, the ReO_x-support interaction determines (together with the reaction environment) the oxidation state of Re which can be further modified by select transition metals such as Pd. However, the oxidation state modification of Re by the transition metal is support defect dependent. Re(+6) is able to catalyze the DODH reaction and is likely the active site in the experimental catalysts. A Re(+7) is likely even more active than Re(+6) but it appears to be challenging to stabilize this Re species under reaction conditions.

4. Conclusions

We performed first principles calculations to understand the deoxydehydration of 1,4-anhydroerythritol (AE) on ReO/CeO₂ and ReO-Pd/CeO₂ catalysts. We started from an ideal support model without oxygen vacancies and a CeO₂(111) facet. *Ab*

initio thermodynamic calculations suggest that the ceria surface is fully-hydroxylated while the structure of the ceria supported Re species is ReO. The established atomistic structures were used to examine the mechanism of the AE deoxydehydration. The removal of the two AE OH groups takes place at a ReO site, converting it to a ReO2 species. The direct reduction of ReO2 by H2 was found to be difficult. Therefore, we proposed an alternative water-facilitated surface hydrogen migration mechanism, which creates two hydrogen vacancies on the hydroxylated surface. For the ReO/ CeO₂ catalyst model the replenishment of hydrogen vacancies through dissociative adsorption of H2 needs to overcome a very high barrier and the direct reduction of ReO2 remains the dominant (but slow) pathway. In the presence of a coadsorbed Pd cluster near the ReO/CeO2, the replenishment of hydrogen vacancies is facile due to rapid hydrogen spillover from the Pd cluster onto the CeO₂ surface. In this context, we identified a pathway involving a ReO(OH) species that is highly efficient for the reduction of ReO2. To disentangle the specific contributions of Pd in the multicomponent catalyst, we investigated a hypothetical case where Pd only catalyzes the replenishment of hydrogen vacancies after a waterfacilitated surface hydrogen migration process, i.e., it is assumed that the properties of the Re species are unaltered since the Pd is far away. This scenario leads to a high DODH activity in a non-aqueous solvent. The activity in liquid water is reduced due to a reduction in the number of active sites at a higher oxygen chemical potential. When Pd is in close proximity to the Re site (but not in direct contact), a MKM suggests a TOF at 413 K for ReO-Pd/CeO₂ that is higher than the one in the ideal case. The increase in activity originates from nearby Pd modifying the oxidation state of Re from +6 to +7, leading to a more facile O-H bond breaking process. The DHF removal was found to be the rate-limiting step for ReO-Pd/CeO₂ (TS4_Pd), different from the case where Pd only serves as a hydrogen spillover catalyst whose rate-limiting step is the O-H bond breaking (TS1). The effective barrier of TS4_Pd is 0.07 eV lower than TS1, leading to the higher TOF of the former reaction path. It should be noted that even in the absence of the promotional effect of Pd, we still predicted an appreciable TOF of $4.33 \times 10^{-3} \text{ s}^{-1}$ at 413 K.

To better account for the properties of an experimental catalyst containing defects, we investigated the effect of oxygen vacancies. In the presence of OV, Re tends to exhibit an OS of +6, mimicking the properties of the abovementioned hypothetical case. The key role of Pd is to dissociate hydrogen and function as a hydrogen spillover catalyst on the ceria surface. Without the continuous supply of surface hydrogen atoms the Re site cannot be regenerated, i.e., the catalytic cycle cannot be closed, and the TOF for the DODH is vanishingly small. When considering the effect of oxygen vacancies on the ceria support, our computational results are consistent with recent experimental observations.

Overall, the combination of oxide support, defects, and nearby metal cluster determine the oxidation state and activity of the Re species. Considering that we find that the DODH activity could be improved if a Re(+7) species could be stabilized (rather than the already active Re(+6) species), there might be room for further improvements of DODH catalysts based on single Re sites.

Conflicts of interest

The authors declare no competing financial interest.

Note from RSC Publishing

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