Catalytic Water Dehydrogenation and Formation on Nickel: Dual Path Mechanism in High Electric Fields

Fanglin Che,^a Jake T. Gray,^a Su Ha,^a Jean-Sabin McEwen^{*abc}

^a*The Gene and Linda Voiland School of Chemical Engineering and Bioengineering, Washington State
University, WA, 99164*

^b*Department of Physics and Astronomy, Washington State University, WA, 99164*

^c*Department of Chemistry, Washington State University, WA, 99164*

Abstract

To better understand the water/Ni electronic interaction relevant to many industrial catalytic processes, we performed a comprehensive investigation of water dehydrogenation-formation on Ni surfaces. Three perspectives were considered: interactions of water (i) over two distinct Ni surfaces, (ii) in the presence of a pre-adsorbed O atom, and (iii) under the influence of different electric fields. The theoretical results showed that Ni(211) lowered the overall reaction energies of water dehydrogenation-formation reactions as compared with Ni(111). A pre-adsorbed O atom largely accelerated the water dehydrogenation reaction on Ni(211). A negative electric field significantly promoted water dehydrogenation processes, while a positive field greatly enhanced water formation processes. Experimental evidence of water consumption and Ni surface compositions verifies these qualitative findings during methane steam reforming under different applied field conditions. Overall, an applied electric field can play a critical role in catalytic reaction dynamics, which is important when designing water-based catalytic processes.

Keywords: Water dehydrogenation-formation; Ni catalytic surfaces; A pre-adsorbed O atom; External electric fields; Transition state theory; Methane steam reforming.

*Corresponding author: Email: js.mcewen@wsu.edu (J.-S. McEwen); Phone: (+1)509-335-8580

1. Introduction

In many industrial catalytic processes, such as hydrocarbon steam reforming reactions ($C_nH_m + nH_2O \rightleftharpoons nCO + (n + \frac{m}{2})H_2$) [1], Sabatier reactions ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) [2], water gas shift ($CO + H_2O \rightleftharpoons CO_2 + H_2$) [3], and the reactions that are relevant to fuel cells or electrocatalysis [4-7], the significance of water is self-evident. Ni-catalyzed hydrocarbon steam reforming reactions and subsequent syngas electrochemical oxidation, which are the main reactions involved in internal reforming solid oxide fuel cell systems (SOFCs), have already received extensive consideration from both academia and industry [8-10]. This is because SOFCs can offer electric power by the direct conversion of chemical energy with high efficiency [11, 12]. Ni-based Sabatier reactions have also been proposed to make methane using excess electricity in a renewable-energy-dominated system [13]. This is an important step for using CO_2 from the atmosphere to generate methane and water [14]. These catalytic processes are always accompanied by adsorption/desorption steps and the dehydrogenation-formation of H_2O under the influence of electric fields. To provide insight into the catalytic mechanisms of these processes over a Ni catalyst, a first-principles investigation of the electronic interaction of water with Ni surfaces is necessary.

Electric fields of the order of one volt per angstrom at the electrode-electrolyte interface are strong enough to induce rearrangements of the electronic orbitals of molecules, particularly at metal surfaces, leading to new phenomena known as field-induced chemistry [15-19]. By manipulating electronic structures of adsorbates, external electric fields may stabilize previously-unstable adsorbed molecules and accelerate heterogeneous catalytic reactions. Moreover, due to the permanent dipole moment of H_2O , in the presence of an

external electric field, H₂O molecules play a significant role in enhancing or suppressing water-involved electrocatalytic reaction pathways [15, 20].

In recent decades, the effects of electric fields on the interaction between water molecules and transition metal surfaces have been studied. Taylor et al. [21] studied the water dehydrogenation at the interface between a Ni(111) surface and an aqueous solution by density function theory (DFT) calculations. Their results showed that anodic and cathodic potentials changed the rotational configurations of water molecules. Anodic surface polarization strengthens the Ni-O interaction, leading to a weakened surface Ni-Ni bond. Saitta et al. [22] presented the influence of an external electric field on the proton conduction of iced water. They observed that the molecular orientations and the hydrogen bond lengths of water were greatly changed in the presence of an electric field on the order of 0.35 V/Å. When the field is stronger than 0.35 V/Å, water molecules were able to dissociate to form H₃O⁺ and set up an ionic current. When they applied an electric field of 1 V/Å, water molecules instantaneously dissociated which also resulted in an ionic flow. Stüve [15] summarized the ionization of water under an interfacial electric field at an atomic level. An electric field significantly affected hydrogen oxidation or evolution, CO oxidation, and oxygen reduction. By increasing the electric field strength on a stepped platinum surface, greater quantities of OH⁻ from an alkaline solution were able to chemisorb onto the surface to form OH_{ads}. As a result, the adsorption energy of a CO molecule decreased by 0.2 ~ 0.3 eV at a hollow site, leading to the acceleration of the CO oxidation [23].

The Neurock group developed a double reference method [21, 24] to generate the simulated electrode potential by adding (subtracting) explicit charges to (from) the

electrode-electrolyte interface [25]. Interestingly, they also related the used charge to the electrode potential in fuel cells and their theoretical results correlate well with the experimental work [26]. The electrode potential equals the energy differences between the calculated work function of the charged system and the absolute normal hydrogen electrode (NHE) from experimental work. In particular, they found that the optimized structures of the water/Pd interface were significantly changed under different applied potentials. For a H-down (H-up) structure of the water layer, they added (subtracted) electrons to (from) the metal slab and polarized the metal slab to be negatively (positively) charged, which corresponds with a simulated negative (positive) field-induced system using the Neugebauer and Scheffler method (NS) [19], since such a model system also includes a metal slab that is negatively charged at one end of the slab and positively charged the other. In this way, it can indirectly relate the electric fields by the NS method to the electrode potential in the double reference method. Additionally, by adding more than 1.5 electrons to the Pd slab, the electrode potential was maintained below $0.5 V_{\text{NHE}}$. In such system, a negatively charged hydride Pd surface was formed, which corresponds to a simulated negatively charged field-induced system using the NS method [5]. The electroreduction of water occurs at such an electrode potential accompanied by the formation of OH^- ions. Similarly, by subtracting more than 1.5 electrons from the Pd slab, the electrode potential was above $1.1 V_{\text{NHE}}$. This system generated a positively charged Pd-OH surface, which corresponds to a positively charged field-induced system. The electrooxidation of water was predicted at such an electrode potential, which was accompanied by the formation of H_3O^+ ions.

Moreover, Rossmeisl et. al. calculated the thermochemical NHE (referring to the vacuum potential level) via DFT calculations. They showed that the calculated absolute NHE was 5.17 V, which is in reasonable proximity of the experimentally determined range of 4.44 V- 4.85 V [27]. However, up until now, field-induced effects on the interactions between H_2O and Ni have remained largely uninvestigated. To increase our understanding of the catalytic reactions occurring during Ni-based internal reforming SOFCs under steam-hydrocarbon co-feed conditions or other water-based electrocatalytic reactions, a comprehensive study of how a presence of electric field affects the adsorption configurations and the dehydrogenation-formation processes of H_2O molecules on Ni surfaces must be performed.

To simulate a more realistic heterogeneous system, we chose the most stable close-packed flat surface, Ni(111) [28], and the simplest stepped surface, Ni(211) [29-31]. Based on transition state theory (TST) calculations, an investigation of the thermodynamic and kinetic properties of the water dehydrogenation on Ni surfaces is fully described from three perspectives: over two distinct Ni surfaces, in the presence of a pre-adsorbed O atom and under the influence of an electric field. The DFT calculations are verified by our corresponding experimental studies of both the water consumption and Ni catalyst surface composition during methane steam reforming processes under different electric field conditions. Information related to the electric field effects on electronic structures, electronic properties analysis of H_2O , OH and O adsorption on Ni surfaces, as well as the formation processes of H_2O from O is given in the SI. This study is expected to greatly improve our understanding of the electrocatalytic dual path mechanisms of water dehydrogenation-formation, and give a better understanding of the catalytic mechanisms

occurring over Ni-based internal reforming SOFCs under steam-hydrocarbon co-feed conditions and other electrochemical reactions where H_2O participates as the main reactant/product species by combining the present results with our previous work [28, 31].

2. Theory

Our DFT calculations use the Perdew-Wang 91 (PW91) exchange correlation functionals [32] at the Generalized Gradient Approximation [33, 34] level in the Vienna *Ab Initio* Simulation Package (VASP). Electrons are described using the projector-augmented wave method in order to solve the Kohn-Sham equations [35]. Both the quasi-Newton algorithm [36] and the conjugate-gradient algorithm are applied to relax the ions into their ground state configurations [37, 38]. For a $p(3\times3)$ [39-41] Ni(111) supercell, we apply a four-layer slab [28] and for a $p(2\times4)$ Ni(211) supercell, a five-layer metal slab is applied [31]. The differences in the adsorption energies of water on Ni(111) in the presence and absence of an external electric field between a 4-layer and a 5-layer Ni slabs are all less than 0.01 eV. The plane-wave basis is expanded to an energy cutoff of 400 eV. We approximate the Brillouin zone integration by a sum of k-points using a $(4\times4\times1)$ Monkhorst-Pack mesh on Ni(111) and a $(5\times3\times1)$ mesh on Ni(211) [42]. With a higher energy cutoff (450 eV) and finer k-points mesh of $(6\times6\times1)$ for Ni(111), the differences in the adsorption energy are only ~ 0.01 eV from our previous work [28]. More details about the computational setup are given in our previous work [28, 31].

In addition, we also calculate the van der Waals corrections (optB88-vdW) [43-47] for field-induced water/metal interactions. The water adsorption energies on Ni(111) are shifted by ~ 0.15 eV and the water dehydrogenation reaction energies are shifted by ~ 0.1 eV with and without electric fields. The electric field trends with regard to the water/metal

interaction are not altered by the van der Waals corrections. Therefore, our entire calculations are performed using the PW91 functional. More details of computational setup are given in the SI.

DFT calculations are able to simulate the interactions of H₂O with the metal surfaces with electric fields. A large potential drop at the electrode/electrolyte interface generates such a large external electric field, on the order of -1 V/Å to 1 V/Å [8, 15, 48]. Here, we assume that the field is uniform inside the electrode/electrolyte interface [49, 50]. To simulate the field-induced system through our DFT calculations, we use the same approach as proposed by Neugebauer and Scheffler [19], wherein the uniform electric fields are generated without adding or removing any charge from the supercell [51]. Regarding the ‘field emissions’ effects [52], our vacuum width is ~11 Å. This leads to a charge density in the vacuum, which is less than the magnitude of the Gibbs’ oscillations (0.001 e/Å³) associated with plane-wave cutoffs (given in the SI Section 1.2).

The adsorption energy (E_{ad}) of molecule **A** is calculated using Eq. (1). The reaction energies (ΔH_{rxn}) of the $A + B \rightarrow C + D$ reaction are calculated in Eq. (2):

$$E_{ad} = E_{(A/slab)} - E_{(slab)} - E_{(A)} \quad (1)$$

$$\Delta H_{rxn} = E_{((C+D)/slab)} - E_{((A+B)/slab)} \quad (2)$$

where $E_{(A/slab)}$, $E_{(slab)}$, and $E_{(A)}$ are the total energy of molecule **A** adsorbed on the periodic slab, the periodic slab, and molecule **A** in the gas phase, respectively. For the $A + B \rightarrow C + D$ reaction, the reaction energy, ΔH_{rxn} , is the energy difference between the reactants and products adsorbed on the periodic slab. When we examine the field-induced adsorption energy of molecule **A** or the $A + B \rightarrow C + D$ field-induced reaction energy, all the energies in Eq.(1) and Eq.(2) are converged in the presence of an electric field. We remark

that in this manuscript we designate the reaction energy barrier before ZPE corrections as E_a and after ZPE corrections as E_a^0 . Similarly, we designate the reaction energy before ZPE corrections as ΔH_{rxn} and the value after ZPE corrections as ΔH_{rxn}^0 .

To examine the transition states (TS) of the water dehydrogenation-formation processes on the Ni surfaces with different electric fields, the nudged elastic band (NEB) [53] and the climbing image nudged elastic band (CINEB) methods [54, 55] are applied. More details are also given in our previous work [28, 31]. Vibrational frequency calculations performed for the stationary points on the potential energy surface ensure that the initial states (IS) and final states (FS) are stable (with no imaginary frequencies) and the TS have only one imaginary frequency. These results are also used to determine the ZPE correction of the IS, FS and TS in the TST. When we examined the vibrational frequencies, both the adsorbates and the uppermost bonded Ni atoms were allowed to relax. Transition state theory [56-58] is used to identify the rate constant (k_f), and the equilibrium constant (K) at the examined temperatures for the water dehydrogenation-formation processes. In Eq. (3), the partition functions are calculated using the harmonic oscillator approximation around the IS and TS on the potential energy surface,

$$k_f = \left(\frac{k_B T}{h}\right) \left(\frac{q^*}{q}\right) e^{-E_a^0 / k_B T} \quad (3)$$

where T is the absolute temperature. k_B and h are the Boltzmann's constant and Planck's constant; q^* and q are the partition functions of the TS and the IS, respectively.

3. Results and Discussion

3.1 Field-Induced Thermodynamic Properties of Water on Ni Surfaces

3.1.1 Field-Induced H₂O Adsorption.

Our DFT calculations investigated the field-induced adsorption of H₂O, OH and O on both Ni surfaces. The adsorption sites on Ni(111) and Ni(211) are labeled in Fig. 1 and the adsorption energies with the corresponding sites are summarized in Table 1. For more details on the adsorption site nomenclature, the reader is referred to our previous work [31]. Based on the errors associated with layer effects, finite k-points mesh, and energy cutoff, all the energies reported in this manuscript are estimated to have an accuracy of 0.01 eV.

When the field is absent, a H₂O molecule prefers to adsorb at a top site with an orientation almost parallel to the Ni(111) surface ($\alpha = 101^\circ$ in Fig. 2(a2)). Via DFT calculations, the adsorption energy of water is very weak, -0.30 eV (Table 1), which is in agreement with the values of -0.36 eV and -0.25 eV in the literature [59, 60]. The corresponding experimental value from the thermal desorption data (TPD) for the first-layer of chemisorbed water is -0.43 eV [61], which correlates well with our results of -0.45 eV for the adsorption energy of a H₂O molecule with van der Waals corrections (given in the SI). For Ni(211) at zero fields (Fig. 2(b2)), a H₂O molecule has slightly stronger adsorption energy of -0.62 eV than that of Ni(111).

Interestingly, an electric field of the order of -1 V/Å to 1 V/Å, can significantly alter the orientation of an adsorbed H₂O molecule on both Ni flat and step surfaces. From Fig. 2, the H-down structure is stable on a negatively charged Ni surface (negative fields), while the H-up structure is favorable when we apply a positive electric field for both Ni(111) and Ni(211). The electric field effects on the adsorption orientation of an isolated H₂O molecule on Ni(111) are similar to both a water monolayer and a water multilayer on Pd(111) with different electrode potentials [24, 62-65].

An external electric field also largely influences the stability of H₂O on both Ni surfaces (Fig. 3(a)). A negative electric field destabilizes H₂O, while a positive electric field strengthens its adsorption. The electric field effects on water adsorption can be explained by frontier molecular orbital theory [62, 63]. With a positive field, the HOMO water orbital (1b₁) has more interactions with the d states of the Ni slab than the scenarios without a field. On the other hand, the water HOMO orbital in the presence of a negative field has almost no overlap with the d states of the Ni slab, which correlates well with the fact that the H-down structure is not stable. The density of states of the water/metal system in the presence of a field can be found in Fig. S4.

Such significant field effects on the water/metal interactions can be visualized via the differential charge density (Fig. 2(e) and Fig. 2(f)). In particular for Ni(111), the differential charge density of H₂O upon adsorption with a negative electric field of -1 V/Å shows that H₂O mainly gains charge from the metal surface (Fig. 2(e1)). However, under such a condition, the transferred charge between H₂O and the metal surface is much less as compared to the scenario without an electric field (Fig. 2(e2)). This correlates well with the fact that water under the field of -1 V/Å is weakly bonded with Ni(111). To clearly show the charge transfer of the H₂O/metal system with a negative field, the differential charge density of this system at a smaller isosurface level is given in Fig. S5. With a positive field, an isolated H₂O molecule on Ni(111) loses more electrons to the surface (Fig. 2(e3)) than the scenario without a field (Fig. 2(e2)). This shows that the increased stability of H₂O on Ni(111) with a positive field is due to a greater number of transferred electrons in the H₂O/metal system. The differential charge density of the water/Ni(111) system correlates well with the literature [62]: A negatively charged H-down configuration for the

water/Pd(111) system is stable at lower potential values (negative fields); while a positively charged H-up structure is more stable at higher potential values (positive fields).

3.1.2. Field-Induced H₂O adsorption with a pre-adsorbed O atom.

The surface coverage of O atoms over a Ni-based anode in the internal reforming SOFCs under the steam-hydrocarbon co-feed conditions could be high. Thus, the dehydrogenation of water in the presence of a pre-adsorbed oxygen atom is another competitive reaction pathway that must be considered [66, 67].

At zero fields, a pre-adsorbed O atom has a different effect on Ni(111) than it does on Ni(211) with regard to the adsorption of H₂O (Fig. 2(c) and Fig. 2(d)). As compared with an isolated H₂O molecule, a H₂O molecule with a pre-adsorbed O atom is more strongly bonded by ~0.2 eV on Ni(111). This increase in binding of water can be better understood by examining the bond length between the H atom of H₂O and the pre-adsorbed O atom, which is only 1.9 Å (Fig. 2(c2)). The pre-adsorbed O atom forms a hydrogen bond with the water molecule on Ni(111), which further strengthens the adsorption of H₂O. For Ni(211), the bond length between the H atom of H₂O and the pre-adsorbed O atom is ~3.5 Å. In this case, there is no hydrogen bond between the pre-adsorbed O atom and the isolated water molecule on Ni(211). Thus, with a pre-adsorbed O atom on Ni(211), a H₂O molecule has similar adsorption energy as compared to when a pre-adsorbed O atom is absent. Overall, a pre-adsorbed O atom greatly stabilizes H₂O adsorption on a Ni flat surface but has nearly no influence on the adsorption of water on a Ni stepped surface.

Additionally, this system maintains the previously-described electric field trends on the adsorption of a H₂O molecule with a pre-adsorbed O atom on Ni(111) and Ni(211) (Fig. 2(c), Fig. 2(d) and Fig. 3(c)) but enlarges the field-induced effects on the adsorption of H₂O

as compared to the ones without a pre-adsorbed O atom. The Ni(211) surface is particularly interesting, as it presents a fifty percent increase in the electric field effects on the H₂O adsorption energy as compared to without the additional O atom. With a pre-adsorbed O atom on Ni(211), the adsorption energy of a H₂O molecule strengthens from -0.03 eV to -0.76 eV when applying an electric field ranging from -1 V/Å to 1 V/Å. This change is 1.5-fold larger than the case without a pre-adsorbed O atom, wherein the H₂O adsorption energies increase from -0.19 eV (-1 V/Å) to -0.67 eV (1 V/Å).

3.1.3. Field-Induced Adsorption of Intermediates of OH and O on Ni.

In the absence of fields, both OH and O adsorb much stronger than water on both Ni surfaces (shown in Table 1). For the intermediate OH on Ni surfaces, the interface dipole moment of O-Ni is much stronger than the one of O-H. Thus, the intermediate OH experiences similar electric field effects as the O species (Fig. 3(c) and (d)). Furthermore, the interface dipole moment of the adsorbates along with the field direction increases the adsorbate/metal charge transfer. As a result, a positive electric field decreases the stability of the intermediates (OH and O) on Ni, while a negative electric field increases their stabilities. In particular, the adsorption stability of OH over Ni(211) is decreased (increased) by ~0.4 eV when an electric field of 1 V/Å (-1 V/Å) is applied. For a such case, the change in the adsorption energy due to electric field (ΔG_{field}) in the construction of the surface Pourbaix diagram would need to be included since such field effects are non-negligible [68]. More information with respect to field-induced adsorption of OH and O species, and their electronic property analysis (projected DOS, differential charge density and Bader charge analysis) are given in the SI Section 2.

3.1.4. Reaction energies of water dehydrogenation-formation processes.

To examine the effects of an external electric field on the thermodynamic properties of the dual path mechanisms of water dehydrogenation-formation on Ni surfaces, one of the key points is the reaction energy (summarized in Table 2). In our corresponding SI, we present the co-adsorption geometries of OH and H; O and H; OH and OH systems.

3.1.4.1 Field-Induced Reaction Energy of the $H_2O \rightleftharpoons OH + H$ Reaction.

The $H_2O \rightleftharpoons OH + H$ reaction is exothermic on Ni(111) and Ni(211) with zero fields, with ΔH_{rxn} values of -0.36 eV and -0.61 eV, respectively. An external electric field on the order of -1 V/Å to 1 V/Å can have significant effects on this reaction (Fig. 4A). For Ni(111), the value of ΔH_{rxn} increases with both a positive and a negative field. A strong negative field can make this reaction energy-neutral instead of exothermic. For Ni(211), the reaction energy monotonically increases from -0.63 eV to -0.21 eV when increasing the field from -1 V/Å to 1 V/Å. Based on the overall energy of this reaction, it is more exothermic and therefore more likely to occur on Ni(211) with a negative field as compared to the same reaction on Ni(111) which is energy-neutral at the same field strength.

3.1.4.2 Field-Induced Reaction Energy of the $OH \rightleftharpoons O + H$ Reaction.

The second step of the water dehydrogenation-formation is the $OH \rightleftharpoons O + H$ reaction. At zero fields, the reaction energy of this reaction is much higher than the $H_2O \rightleftharpoons OH + H$ reaction, with ΔH_{rxn} values of -0.18 eV (Ni(111)) and 0.19 eV (Ni(211)), respectively. For Ni(111), an external field shifts the OH dehydrogenation reaction from an exothermic to an endothermic process (Fig. 4B). On the other hand, the OH dehydrogenation reaction is always endothermic on Ni(211) regardless of the field strength. This reaction is therefore more energetically favorable on Ni(111) with a negative field.

3.1.4.3 Field-Induced Reaction Energy of the $H_2O + O \rightleftharpoons OH + OH$ reaction.

As briefly explained in Section 3.1.2, a large amount of O^{2-} species coming from the cathode in a SOFC to the anode can pre-adsorb on the Ni catalysts. At zero fields, Table 2 shows that a pre-adsorbed O atom increases the water dehydrogenation reaction energy to 0.23 eV ($\Delta H_{\text{rxn}} = -0.36$ eV without a pre-adsorbed O atom) on Ni(111). Such an increase of the reaction energy of water dehydrogenation on Ni(111) is likely due to the hydrogen bond between the water and the pre-adsorbed O atom that needs to be broken in the dehydrogenation reaction. The presence of a positive electric field facilitates the breaking of such a hydrogen bond in the $H_2O + O \rightleftharpoons OH + OH$ reaction on Ni(111): The reaction energy monotonically decreases from 0.47 eV to 0.18 eV when increasing the field strength from -1 V/Å to 1 V/Å. On the other hand, the ΔH_{rxn} value monotonically increases from -0.50 eV to -0.17 eV when increasing the electric field from -1 V/Å to 1 V/Å on Ni(211). With regard to the reaction energy of both the $H_2O + O \rightarrow OH + OH$ and $H_2O \rightarrow OH + H$ reactions, the most exothermic dehydrogenation reaction for water is the $H_2O \rightarrow OH + H$ reaction on a Ni(211) surface in the presence of a negative field of -1 V/Å. The following sections will analyze why an external electric field has such a significant influence on the water/metal interactions.

3.1.5 Discussions of electric field effects on the water/metal interactions.

3.1.5.1. Electric field effects on adsorption structures

As can be seen from Fig. 2(a)-(d), an external electric field greatly alters the adsorption structure of H_2O on both Ni surfaces. The following discussion seeks to elucidate the reason for the varying electronic structures of H_2O with different electric fields. A positive electric field pointing away from the metal surface from an artificial

dipole layer (the red arrow in Fig. 2(e3)) polarizes the bonded Ni surfaces with a partial positive charge. Thus, the O atom of the water molecule, which has a partial negative charge, is bonded more strongly to the surface due to attractive electrostatic forces. On the other hand, a H atom of the water molecule, which has a partial positive charge, shifts further away from the surface because of repulsive electrostatic forces (H-up structures). A negative field, pointing towards the surface, has a correspondingly opposite effect on the electronic structures of a H₂O molecule on the Ni surfaces (H-down structures).

3.1.5.2. Discussions of electric field effects on adsorption energies

From Section 3.1.1-3.1.4, we have established that a high electric field can significantly alter the adsorption energies of isolated H₂O, OH, and O species and a H₂O molecule with a pre-adsorbed O atom. In the presence of a uniform electric field (F), we can expand the total energy (E) in Taylor series (Eq. (4)) [50, 69-72].

$$E = E_0 + (\partial E / \partial F)_{F=0} F + \frac{1}{2} (\partial^2 E / \partial F^2)_{F=0} F^2 + \dots \quad (4)$$

where all the derivatives are evaluated at $F = 0$ V/Å and E_0 is the total energy without an electric field. According to the Hellmann-Feynman theorem, the derivative of the energy with respect to any parameter is the expectation value of the derivative of the Hamiltonian with respect to that parameter [73]. Using such definitions, the following Taylor series for the adsorption system as a function of an electric field (Eq. (5)) can be written

$$E_{ad} = E_{ad0} - \Delta d_{F=0} F - \frac{1}{2} \Delta \alpha_{F=0} F^2 + \dots \quad (5)$$

where E_{ad0} is the adsorption energy in the absence of a field and $\Delta d_{F=0}$ (or $\Delta \alpha_{F=0}$) is the dipole moment (or polarizability and surface capacitance [27, 69]) difference between the

system with adsorbates on a metal slab and the corresponding non-interacting system (clean surface and adsorbates in the gas phase). The values of $\Delta d_{F=0}$ and $\Delta \alpha_{F=0}$ for the involved species are summarized in Table 3. In particular, for the field-induced water adsorption on a metal surface, the third order derivative of the energy (the electrochemical change of the Hessian matrix) needs to be included so as to capture the field dependence of a water molecule. The value of the third order derivative is given in Table S3 in the SI.

Combining Fig. 3 and Table 3, we notice that the greatest contribution to the change of the adsorption energy dependence on an external electric field comes from the magnitude of $\Delta d_{F=0}$. For example, the $\Delta d_{F=0}$ values of a H₂O molecule on Ni(111) and Ni(211) are 0.25 eV·Å/V and 0.16 eV·Å/V, respectively, which are about two times greater than the largest $\Delta d_{F=0}$ values for a CH₃ fragment on each corresponding surface[26, 28, 31]. These results correlate well with the fact that the electric field has larger effects on the adsorption energy of a H₂O molecule than those on a CH₃ fragment on Ni(111) and Ni(211). Additionally, the magnitude of $\Delta d_{F=0}$ for H₂O with a pre-adsorbed O atom on Ni(211) is 0.1 eV·Å/V larger than that of Ni(111), which again verifies that the field-induced effects on the adsorption energy of H₂O with a pre-adsorbed O atom on Ni(211) are much more significant than the corresponding scenario on Ni(111). Overall, by comparing the different $\Delta d_{F=0}$ values for the adsorption systems examined in this paper, a OH molecule on Ni(211) has the largest magnitude of $\Delta d_{F=0}$, -0.35 eV·Å/V and hence the largest field dependence. In this way, we can predict how an electric field affects the adsorption energy of adsorbates on metal surfaces if we know the effective dipole moment ($\Delta d_{F=0}$) and the effective polarizability and surface capacitance ($\Delta \alpha_{F=0}$). Similarly, the Taylor series can be applied to the field dependence of ΔH_{rxn} for the water dehydrogenation. For example, as can be seen

from Fig. 4, the $OH \rightarrow O + H$ reaction on Ni(111) has the largest electric field effects on its reaction energies as compared to the other examined reactions, which correlates well with the largest corresponding values of $\Delta d_{F=0}$.

3.2 Field-Induced Dual Path Mechanisms of Water Dehydrogenation

In Section 3.1, an external electric field, on the order of $-1 \text{ V/\AA}$ to $1 \text{ V/\AA}$, was shown to significantly alter the dual path mechanisms of water dehydrogenation-formation. We further studied how an electric field influences the kinetic properties of this process by using transition state theory (TST), including the energy barriers, the rate constants, and the equilibrium constants at certain temperatures (summarized in Table 4). We note that the equilibrium constant is dependent on the strength of the electric fields as shown by the Van't Hoff equation ($\Delta M / RT = \partial \ln K / \partial F$) where ΔM represents the partial molar energy related to the change in the electric moment in the reaction [17, 74]. The examined temperature is 463 K since it is the typical temperature for the low-temperature water gas shift reaction [75, 76], in which water dehydrogenation plays an important role. Additionally, the temperature of 523 K is chosen because there is a recent interest to operate the methane steam reforming reaction below its typically required temperature of 873 K by applying the external electric field. Such a low temperature operation can significantly decrease the undesired side reactions (e.g., coking). For example, Sekine et al. examined experimentally the water gas shift reaction and the methane steam reforming reaction [1, 76, 77] and found that an external electric field significantly increased the conversion of reactants over different metal catalysts [1, 76, 77]. We compared our calculations with such experiments and other theoretical calculations that are available in the literature. In Section 4 of the SI, we show both the electric fields and a pre-adsorbed O

atom also have significant effects on the dual path mechanisms of the water formation processes.

3.2.1 The $H_2O \rightarrow OH + H$ reaction.

Our analysis shows that the water dehydrogenation mechanism to form a hydroxyl group goes through a local minimum and separates into two segments on both Ni(111) and Ni(211): water dehydrogenation (Fig. 5A-D and Fig. 6A-D) and hydrogen surface diffusion (Fig. 5D-F and Fig. 6D-F). For the surface diffusion for the H atom on both Ni surfaces, the E_a^0 value is only 0.1 eV. The water dehydrogenation reaction is exothermic, with an E_a^0 value of 0.69 eV on Ni(111) and 0.81 eV on Ni(211). With respect to the activation on Ni(111), our result is in agreement with the 0.75 eV value from Mohsenzadeh et al. [59]. The rate constant at 463 K without an electric field is $1.1 \times 10^4 \text{ s}^{-1}$, which also correlates well with the rate constant of $2.0 \times 10^4 \text{ s}^{-1}$ calculated by Mohsenzadeh et al. [59]. For the water dehydrogenation segment, Ni(211) appears to be less kinetically active than Ni(111), with a rate of $5.5 \times 10^2 \text{ s}^{-1}$ in the absence of a field at 463 K. Nevertheless, the equilibrium constant is over 10^4 at both surfaces. Therefore, the $H_2O \rightarrow OH + H$ reaction is significantly energetically and kinetically more favorable than its reverse reaction.

An external electric field doesn't largely alter the hydrogen surface diffusion segment on both Ni surfaces. Thus, we mainly describe the field effects pertaining to the water dehydrogenation segment. A positive electric field significantly increases the energy barriers of the $H_2O \rightarrow OH + H$ reaction and largely decreases the rate constants as compared to the case without an electric field, suggesting that such a strong field can greatly suppress this reaction. Particularly, on Ni(111), the rate constant of this reaction at 463 K decreases by a factor of 3 as compared to the case in the absence of a field. It is also

worth mentioning that this reaction on Ni(211) with a positive field becomes energy-neutral and the equilibrium constant decreases by 3 orders of magnitude at both temperatures when compared to the field absent case. Upon application of a negative field, the magnitude of the rate constants of this reaction increases on both Ni surfaces. In particular for Ni(211), the energy barrier significantly decreases by ~ 0.2 eV and the rate constants at both 463 K and 523 K increase by a factor of 3 for the same reaction at zero fields. Therefore, the $H_2O \rightarrow OH + H$ reaction on Ni catalysts is notably accelerated with a negative electric field. Additionally, for the $H_2O \rightarrow OH + H$ reaction in the presence of a negative field, this reaction is more favorable on Ni(211) than that on Ni(111). The geometries and vibrational modes along with the water dehydrogenation processes are summarized in the SI.

3.2.2 The $OH \rightarrow O + H$ reaction.

Fig. 7 and Fig. 8 present the rate-limiting step of the complete water dehydrogenation reaction on Ni(111) and Ni(211): the $OH \rightarrow O + H$ reaction. In the absence of a field, this reaction on Ni(111) is exothermic and experiences an E_a of 0.97 eV. For Ni(211), the $OH \rightarrow O + H$ reaction passes over two local minima (Fig. 8C and Fig. 8D), so we separated this reaction into three segments: OH dehydrogenation, oxygen surface diffusion and hydrogen surface diffusion. The main segment (OH dehydrogenation) is endothermic on Ni(211), with an energy barrier of 0.86 eV. For oxygen surface diffusion, it has a ΔH_{rxn}^0 value of -0.26 eV and no energy barriers. For the hydrogen atom diffusion, it has an E_a^0 value of 0.21 eV and a ΔH_{rxn}^0 value of -0.09 eV. Also, the rate constants of the $OH \rightarrow O + H$ reaction are enhanced more significantly than ones for the $H_2O \rightarrow OH + H$ reaction as the temperature is increased.

Similarly to the $H_2O \rightarrow OH + H$ reaction on both Ni surfaces, the $OH \rightarrow O + H$ reaction is also significantly suppressed by a positive electric field and largely accelerated by a negative electric field. Upon the application of a positive electric field, the E_a^0 value of this reaction increases by ~ 0.2 eV on both surfaces. The corresponding rate constants and equilibrium constants decrease by two orders of magnitude at the examined temperatures on the Ni catalysts as well. On the other hand, a negative field has an opposite effect. The rate constants and equilibrium constants are enhanced by over two orders of magnitude at both 463 K and 523 K upon application of a negative field. However, since the equilibrium constants of this reaction on Ni(211) at the examined temperatures of 463 K and 523 K with and without an external electric field are much smaller than 1, we can conclude that the dehydrogenation of OH is less likely to occur on Ni(211) than the formation of OH. Moreover, since the equilibrium constant on Ni(111) for the dehydrogenation of OH with a negative electric field (at 463 K, $K = 2.6 \times 10^6$) is much larger than on Ni(211), the Ni(111) surface is much more active for the dehydrogenation of OH as compared to Ni(211) surface.

3.2.3 The $H_2O + O \rightarrow OH + OH$ reaction.

At zero fields, with a pre-adsorbed O atom, the energy barriers of the $H_2O + O \rightarrow OH + OH$ reaction are notably decreased by ~ 0.4 eV on both Ni surfaces (Fig. 9 and Fig. 10). However, for Ni(111), the equilibrium constant of this reaction is only 7.0×10^{-4} at 463 K, indicating that the formation of a H_2O molecule from two OH molecules is more energetically favorable than the $H_2O + O \rightarrow OH + OH$ reaction. Overall, in the absence of an external electric field on Ni(111), the reaction activity order follows: $H_2O \rightarrow OH + H > OH \rightarrow O + H > H_2O + O \rightarrow OH + OH$. The most favorable mechanism on Ni(111) for complete water dehydrogenation with no fields is the

$H_2O \rightarrow OH + H \rightarrow O + 2H$ reaction. We also remark that Yoo et al. found a promoting effect of oxygen species on the FCC(111) surface for numerous metals during the O-H bond activation, which can be predicted by establishing a transition state scaling (TSS) relations for the dehydrogenation reaction [78]. We calculated the TSS relations for the water dehydrogenation in the presence and absence of a pre-adsorbed O atom on a Ni(111) surface. Our results show that the O-assisted reaction pathway on Ni(111) has significantly larger reaction energies as compared to when O is absent. This correlates well with our conclusion that the $H_2O \rightarrow OH + H$ reaction is more favorable than the $H_2O + O \rightarrow OH + OH$ reaction on Ni(111). On the other hand, for Ni(211), the rate constants of the $H_2O + O \rightarrow OH + OH$ reaction reaches up to $\sim 10^7 \text{ s}^{-1}$ at 463 K, which is over 10^5 times larger than that of the $H_2O \rightarrow OH + H$ reaction at such conditions. The equilibrium constants of the $H_2O + O \rightarrow OH + OH$ reaction on Ni(211) are over 10^4 at the examined temperatures. As a result, a pre-adsorbed O atom largely accelerates the water dehydrogenation processes on Ni(211).

An external electric field has considerable effects on the $H_2O + O \rightarrow OH + OH$ reaction pathway as well, including the geometric configurations along with the reaction pathway, the energy barriers, rate constants, and equilibrium constants (Table 4). More details of the reaction structures pertaining to the reaction pathway in the presence and absence of an external electric field are given in Table S9 – S14 in the SI. Upon application of a positive electric field, even though the energy barriers are increased and the reaction rate constants of this reaction are slightly decreased, this reaction is still much faster than the $H_2O \rightarrow OH + H$ reaction and the $OH \rightarrow O + H$ reaction scenarios under the same conditions. However, the negative field effects between the Ni(111) and the Ni(211) system

are quite different on the water dehydrogenation with a pre-adsorbed O atom. For Ni(111), a negative electric field has similar effects as those in the presence of a positive field for this reaction, in which it increases the energy barriers and decreases the rate constants. For Ni(211), a negative electric field increases the rate constants by a factor of 3 and the equilibrium constant is 10-fold larger than the scenario without an electric field.

In summary, for the dehydrogenation of water on a Ni(111) surface with different electric fields, the $H_2O + O \rightarrow OH + OH$ reaction has an equilibrium constant that is smaller by a factor of $\sim 10^8$ than the $H_2O \rightarrow OH + H$ reaction at the examined temperatures of 463 and 523 K. This indicates that a pre-adsorbed OH molecule greatly accelerates the water formation rather than dehydrogenation. Additionally, a negative electric field greatly accelerates both the $H_2O \rightarrow OH + H$ reaction and the $OH \rightarrow O + H$ reaction on Ni(111). Therefore, the $H_2O \rightarrow OH + H \rightarrow O + 2H$ reaction with a negative electric field is the most favorable mechanism on Ni(111). For a Ni(211) surface, the $H_2O + O \rightarrow OH + OH$ reaction with a negative electric field is the most favorable pathway for partial water dehydrogenation. An external positive electric field greatly inhibits all examined mechanisms during the water dehydrogenation process on both Ni surfaces. The following section will discuss how the two Ni surfaces, a pre-adsorbed O atom, and electric fields influence the dual path mechanisms of the water dehydrogenation processes.

3.2.4. Discussions of the water dehydrogenation reactions from three different perspectives.

3.2.4.1. Various Ni surfaces

Fig. 11 (a) and (b) show the dual path mechanisms of water dehydrogenation: the $H_2O \rightarrow OH + H \rightarrow O + 2H$ reaction (Mechanism 1) and the $H_2O + O \rightarrow 2OH \rightarrow 2O + 2H$

reaction (Mechanism 2) on Ni(111) and Ni(211) without an electric field. We remark that the adsorption of a H_2O molecule in Mechanism 2 is with respect to a pre-adsorbed O atom surface (see caption of Table 1), so that we can directly compare the energy profiles of both mechanisms. We assume that the dissociated products in each reaction step are infinitely separated from each other when constructing the energy profiles. For example, the dissociation energies for the $H_2O \rightarrow OH + H$ reaction (E_{diss}^1) and the $H_2O + O \rightarrow OH + OH$ (E_{diss}^2) reaction are given by:

$$E_{diss}^1 = E_{(OH/slab)} + E_{(H/slab)} - 2E_{(slab)} - E_{(H_2O)} \quad (6)$$

$$E_{diss}^2 = 2E_{(OH/slab)} - E_{(slab)} - E_{(O/slab)} - E_{(H_2O)} \quad (7)$$

From Fig. 11(a) and (b), it is clearly seen that the $H_2O \rightarrow OH + H \rightarrow O + 2H$ reaction is more exothermic on a step surface with a smaller overall energy barrier as compared to a flat surface. Additionally, the initial adsorption of a H_2O molecule is more strongly bonded to a Ni(211) surface as compared to a Ni(111) surface. However, the $OH \rightarrow O + H$ reaction on Ni(211) is an endothermic reaction with an equilibrium constant that is much smaller than unity, suggesting that a OH molecule is less likely to completely dehydrogenate to form an O atom on Ni(211). Since the rate constants and equilibrium constants for both the $H_2O \rightarrow OH + H$ reaction and the $OH \rightarrow O + H$ reaction on Ni(111) are very large, the $H_2O \rightarrow OH + H \rightarrow O + 2H$ reaction is more likely to occur on Ni(111) than on Ni(211) for the complete water dehydrogenation processes.

3.2.4.2.A pre-adsorbed O atom.

The water dehydrogenation processes of mechanism 2 is of particular interest, as a pre-adsorbed O atom can also stabilize the adsorption of a H_2O molecule on a Ni(111)

surface. With a pre-adsorbed O atom, the energy barriers of the water dehydrogenation reaction are much smaller on both Ni(111) and Ni(211) than without. The corresponding rate constants of the $H_2O + O \rightarrow OH + OH$ reaction on both Ni(111) and Ni(211) are also much larger compared to the $H_2O \rightarrow OH + H$ reaction at the same temperature. However, the equilibrium constant of the $H_2O + O \rightarrow OH + OH$ reaction on Ni(111) is only 7.0×10^{-4} at 463 K, suggesting a pre-adsorbed O atom significantly accelerates its reverse reaction (the formation of a H_2O molecule from two OH molecules on Ni(111)) instead of the water dehydrogenation reaction. Therefore, with a pre-adsorbed O atom on Ni(211), the partial water dehydrogenation reaction (only forming OH species) is more favorable.

3.2.4.3. Electric field effects.

Fig. 11(c) and (d) show how an external electric field influences the energy profiles of the $H_2O + O \rightarrow 2OH \rightarrow 2O + 2H$ reaction and the $H_2O \rightarrow OH + H \rightarrow O + 2H$ reaction on both Ni(111) and Ni(211). For a H_2O molecule with and without a pre-adsorbed O atom, a positive electric field of 1 V/Å strengthens its adsorption energy, while a negative electric field weakens its adsorption energy on both Ni surfaces. Moreover, an external electric field changes the adsorption energy of a H_2O molecule on Ni(211) to a greater extent than on Ni(111). Interestingly, a pre-adsorbed O atom also greatly enlarges the electric field effects on the H_2O molecule adsorption energies on the two Ni surfaces. Although a positive electric field increases all the energy barriers of the water dehydrogenation mechanisms on both Ni(111) and Ni(211), the most energetically favorable pathway is the $H_2O + O \rightarrow 2OH \rightarrow 2O + 2H$ mechanism with a positive field due to the corresponding increased stability of a H_2O molecule under such conditions. On the other hand, a negative electric field has an opposite effect on the energy profiles of the dual path mechanisms of

water dehydrogenation processes compared with a positive electric field. Therefore, the stability of the adsorption of a H₂O molecule on both Ni surfaces has a significant effect on the overall energy profile of the water dehydrogenation processes.

3.3 Experimental Evidence

Recent experimental work using the methane steam reformation reaction (MSR) appears to validate many of the findings presented in this manuscript. Both the kinetics of H₂O dehydrogenation during MSR and Ni catalyst surface composition were determined under applied electric fields.

3.3.1 Experimental MSR setup.

A catalyst consisting of porous Ni foam (95%, GoodFellow) modified using Ni micro-particles (90 µm diameter, 99.8%, Alfa Aesar) to increase the effective electric field at the surface of the catalyst was used for all tests. This was created by sintering the Ni micro-particles to the foam under a continuous flow of H₂/Ar at 850°C. Catalysts were placed in a quartz flow-through tube reactor (Quartz Scientific, 1 cm inner diameter) and an electric potential of ±200V was supplied using a DC power source (VOLTEQ HY20010EX) connected directly to the catalyst via silver wire (99.9%, Alfa Aesar). Reaction rates were determined by analyzing the effluent gas composition using gas chromatography (SRI 8610C). The surface coverage of H₂O and OH species over the post-reaction catalyst samples was estimated from their x-ray photoelectron spectroscopy (XPS, Kratos AXIS-165, AlK α X-ray anode) measurements.

MSR was performed at 800°C using a feed stream consisting of H₂O and CH₄ at a molar ratio of 2:1. The reactor temperature was maintained using a ceramic furnace with a resistive heating coil from Watlow controlled by a Barnant PID temperature controller. An

Omega K-type thermocouple was placed in direct contact with the catalyst to ensure the catalyst temperature was controlled as precisely as possible and to avoid Joule (resistive) heating of the catalyst upon application of a potential. The methane flow rate was controlled using an AALBORG rotameter manifold, while water was introduced to the reactor via syringe pump (Cole Parmer). Water was vaporized and both reactants were allowed to mix over an inert silicon carbide preheating section maintained at 200°C. Effluent gases passed through a cold trap where water was removed before it was sent to the GC for the gas composition or to an Alltech digital flowmeter for flow rates. The catalyst was pretreated with H₂ gas for ten minutes and allowed to equilibrate/purge for a half hour between the applied electric bias changes to ensure similar conditions for all tests.

Catalysts were subjected to MSR conditions under different electric fields for five continuous hours before the reaction was quenched under Ar and the O 1s peaks were recorded via XPS at room temperature. The instrument was calibrated using both the Au 4f_{7/2} peak at 84.0 eV and the Ag 3d_{5/2} peak at 368.3 eV. Spectra for each of the samples were deconvoluted using CasaXPS to quantify individual oxygen species on the surface.

3.3.2 Experimental results analysis.

XPS data presented in Fig. 12 shows a clear trend of increasing H₂O surface coverage with increasingly positive electric field, from only 14.6% under a negative field to 35.2% under a positive field. Regarding the OH surface coverage under the different applied electrical bias, it shows an opposite trend compared to that of H₂O. Thus, its surface coverage decreases from 14.5% to 5.3% as the applied electrical bias changes from negative to positive values. This experimental result correlates well with the theoretical results that by increasing the electric fields from negative to positive, the adsorption energy

of H₂O on both Ni(211) and Ni(111) is monotonically strengthened and the adsorption energy of OH on Ni surface is monotonically weakened (Fig. 3(a) and (c)). This result also supports the finding that the adsorption of an isolated H₂O molecule is similar to an extended water layer over metal surfaces [21, 24]. Furthermore, from the theoretical analysis in Section 3.2, we conclude that the formation of the hydroxyl groups during water dehydrogenation ($H_2O + O \rightarrow OH + H$) on Ni(211) is the most active reaction. For this reaction, the activation energy barriers are significantly decreased in the presence of a negative electric field but largely increased with a positive electric field (Table 4). In the presence of a positive electric field, the rate constant of the $H_2O + O \rightarrow OH + H$ reaction on Ni(211) (at 800 °C) is decreased by two orders of magnitude as compared to the negative electric field case. This trend is in good agreement with the XPS results which show that the hydroxyl group coverage decreased from 14.5% in a negative field and to just 5.34% in a positive field. Also, the rate constant of this reaction without an electric field is 1.5 times larger than the one with a positive electric field according to our computational data. This again corresponds well with the surface coverage results from the XPS measurements that the hydroxyl group coverage is slightly larger than the case with a positive electric field.

The water consumption rates (given in Fig.12(b)) were collected for both the Ni foam itself and the micro-particle-augmented Ni foam catalyst. This was done to highlight the importance of surface curvature on surface electric fields. No change was noted in the rate of H₂O decomposition on the Ni foam ($p \gg 0.1$), while the rate increased by around 20% in the presence of an applied electric field for the micro-particle-augmented catalyst ($0.01 < p < 0.05$). Here, the p-value represents a probability that is used for carrying out a

statistical significance test. A statistical significance results in a lower p-value. This is expected to improve significantly with a nanoparticle-augmented surface, which is still being developed. The reaction rate data also correlates well with the DFT calculations that negative fields accelerate the water dehydrogenation as compared with the reaction rates in the absence of an applied field.

4. Conclusion

We thoroughly studied the interaction of H_2O with two different Ni surfaces from three different perspectives: over two distinct Ni surfaces, in the presence and absence of a pre-adsorbed O atom, and influenced by different electric fields.

For the complete water dehydrogenation process, the $H_2O \rightarrow OH + H \rightarrow O + 2H$ reaction on Ni(111) is more likely to occur than the corresponding reaction on Ni(211). A pre-adsorbed O atom strengthens H_2O adsorption on Ni(111). Also, it promotes partial water dehydrogenation processes that are more thermally and kinetically favorable than the ones without a pre-adsorbed O atom. For a partial dehydrogenation of H_2O into OH, the $H_2O + O \rightarrow OH + OH$ reaction is more likely to occur on Ni(211) since it has lower energy barriers, higher rate constants and higher equilibrium constants at the examined temperatures of 463 K and 523 K than the same reaction on Ni(111) under such conditions. When examining the effect of a strong external electric field on the dual mechanisms of water dehydrogenation-formation processes, we found that its presence not only largely influences the adsorption of water but also the thermodynamic and kinetic properties of the mechanisms. A positive electric field strengthens the water adsorption but suppresses the water dehydrogenation reactions, while a negative electric field has an opposite effect.

In summary, we conclude that for the complete dehydrogenation of a H_2O molecule into an O atom, the $\text{H}_2\text{O} \rightarrow \text{OH} + \text{H} \rightarrow \text{O} + 2\text{H}$ reaction on Ni(111) in the presence of a negative field is the most favorable pathway. For the partial dehydrogenation of H_2O into OH, the $\text{H}_2\text{O} + \text{O} \rightarrow \text{OH} + \text{OH}$ reaction pathway on a Ni(211) surface with a negative electric field is the most favorable pathway. These findings are validated by the XPS analysis of post-reaction Ni catalytic surface and water consumption rate during MSR under different applied fields. For the partial hydrogenation of an O atom only to a OH molecule, the $\text{O} + \text{H} \rightarrow \text{OH}$ reaction in the presence of a positive electric field on Ni(211) is the most favorable one. For the complete hydrogenation of O to H_2O , it is more likely to occur on a Ni(111) surface with the $2\text{O} + 2\text{H} \rightarrow \text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$ mechanism in the presence of a positive electric field. Overall, it is crucial to choose the direction of an external electric field and the Ni surface types based on which specific reactions are desired.

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Table 1. Summary of the Adsorption Energy (E_{ad}) for the Isolated O, OH, and H₂O Species and a H₂O Molecule with a Pre-adsorbed O Atom on Ni(111) and Ni(211)

Ni(111)	H ₂ O_ E_{ad} (eV)	Site	H ₂ O ^O _ E_{ad} (eV)	Site	OH_ E_{ad} (eV)	Site	O_ E_{ad} (eV)
top	-0.30 , -0.36 ^a , -0.25 ^b , -0.43 ^[Exp.]	H₂O(top)_ O(fcc)	-0.49	top	-3.31, 3.21 ^c	top	-3.95, -3.78 ^a ,
				Bridge	-3.31, -3.03 ^b , -3.69 ^c		-3.69 ^b
fcc	-0.22, -0.38 ^a , -0.11 ^b	H ₂ O(top)_	-0.37	fcc	-3.50 , -3.14 ^b , -3.90 ^c	fcc	-5.83 , -5.56 ^a ,
hcp	-0.22, -0.38 ^a , -0.11 ^b	O(hcp)		hcp	-3.40, -3.08 ^b , -3.90 ^d	hcp	-5.70, -5.43 ^a ,
							-5.40 ^b
Ni(211)	H ₂ O_ E_{ad} (eV)	Site	H ₂ O ^O _ E_{ad} (eV)	Site	OH_ E_{ad} (eV)	Site	O_ E_{ad} (eV)
St	-0.54	H ₂ O_(SLb)	-0.44	Sb2	-4.03	Sb	-5.74
Lb	-0.21	_O (SUh1)		Sb1	-4.01	Lb	-5.04
Ub	-0.17	H ₂ O(SLb)_	-0.39	SLb	-3.33	SLb	-5.68
		O(SUh2)					
SLb	-0.62, -0.49^d	H ₂ O(St)_O (Sb)	-0.40	SUh1	-3.73	SUh1	-6.01
ULh2	-0.41	H₂O(St)_O (SUh1)	-0.55	SUh2	-3.45	SUh2	-5.75
S4	-0.36	H ₂ O(SLb)_	-0.44	ULh1	-3.14	ULh1	-5.49
		O(SUh1)		ULh2	-2.98	ULh2	-5.47
^a from Ref.[59]; ^b from Ref.[60]; ^c from Ref.[79]; ^d from [80]; ^[exp.] from [61]						S4	-5.68

H₂O^O: The E_{ad} for H₂O with a pre-adsorbed O atom is calculated by $E_{ad} = E_{((H_2O+O)/slab)} - E_{(O/slab)} - E_{(H_2O)}$

Table 2. Summary of Reaction energies (ΔH_{rxn}) with various final states configurations for different water dehydrogenation reactions on Ni(111) and Ni(211).

Ni(111)	OH, H	O, H	OH, OH		
Sites	ΔH_{rxn} (eV)	Sites	ΔH_{rxn} (eV)	Sites	ΔH_{rxn} (eV)
fcc, fcc	-0.33	fcc, fcc	-0.13	fcc, fcc	0.33
fcc, hcp	-0.36	fcc, hcp	-0.18	fcc, hcp	0.39
hcp, fcc	-0.27	hcp, fcc	-0.07	hcp, hcp	0.52
hcp, hcp	-0.21	hcp, hcp	0.01	fcc, bri	0.23
Ni(211)	OH (Sb2), H	O (SUh1), H	OH, OH		
Sites	ΔH_{rxn} (eV)	Sites	ΔH_{rxn} (eV)	Sites	ΔH_{rxn} (eV)
SUh1	-0.61	SUh1	0.26	Sb1,Sb1	-0.41
SUh2	-0.54	SUh2	0.24	SUh1,Sb1	-0.28
ULh1	-0.60	ULh1	0.24	Sb2, Sb1	-0.42
ULh2	-0.57	ULh2	0.26	Sb2, Sb2	-0.37
S4	-0.48	S4	0.19	SUh1,Sb2	-0.23

Table 3. Summary of the effective dipole moment ($\Delta d_{F=0}$ in units of $\text{eV}\cdot\text{\AA}/\text{V}$) and the effective surface polarizability and capacitance ($\Delta\alpha_{F=0}$ in units of $\text{\AA}^2/\text{V}$) values of the species involved in the water dehydrogenation-formation processes on Ni(111) and Ni(211) (in parenthesis).

Species	$\Delta d_{F=0}$	$\Delta\alpha_{F=0}$	Species	$\Delta d_{F=0}$	$\Delta\alpha_{F=0}$
H₂O	0.25 (0.16)	-0.154 (-0.30)	OH, H	0.08 (-0.24)	-0.52 (-0.31)
OH	-0.09 (-0.35)	-0.048 (-0.02)	O, H	-0.34 (-0.11)	-0.06 (-0.11)
O	-0.08 (-0.13)	-0.197 (0.20)	OH, OH	0.13 (-0.17)	-0.19 (-0.18)
H₂O^o	0.21 (0.34)	0.400 (0.40)			
Note: H₂O^o represents the adsorption of a H₂O molecule with a pre-adsorbed O atom					

Table 4. The energy barriers, reaction energies, rate constants, and equilibrium constants for water dehydrogenation processes with different electric fields.

Reaction on Ni(111)	F(V/ Å)	E _a /E _a ⁰ (eV)	$\Delta H_{\text{rxn}}/\Delta H_{\text{rxn}}^0$ (eV)	k _f (s ⁻¹) @ 463 K	K @ 463 K	k _f (s ⁻¹) @ 523 K	K @ 523 K
<i>H₂O(top) → OH(fcc) + H(hcp)</i>	1	1.26/1.02	-0.18/-0.30	13.1	1.1 × 10 ³	2.3 × 10 ²	4.7 × 10 ²
Fig. A to Fig. 5D	0	0.90/0.69	-0.32/-0.42	1.1 × 10 ⁴	3.5 × 10 ⁴	8.2 × 10 ⁴	1.1 × 10 ³
TS: OH(top), H(fcc)	-1	0.95/0.74	0.04/-0.07	1.3 × 10 ⁴	1.9	1.1 × 10 ⁵	1.7
<i>OH(fcc) + H(fcc) → OH(fcc) + H(hcp)</i>	1	0.12/0.08	-0.04/-0.04	4.1 × 10 ¹⁰	1.1	4.1 × 10 ¹⁰	1.0
Fig. 5D to Fig. 5F	0	0.12/0.10	-0.03/-0.05	7.1 × 10 ¹¹	5.1	1.0 × 10 ¹²	4.6
TS: OH(fcc), H(bri)	-1	0.13/0.11	-0.03/-0.03	7.8 × 10 ¹¹	3.0	1.1 × 10 ¹²	2.7
<i>OH(fcc) → O(fcc) + H(hcp)</i>	1	1.42/1.25	0.19/0.07	0.7	0.3	29.2	0.3
Fig. 7A to Fig. 7C	0	1.13/0.97	-0.18/-0.27	9.0 × 10 ²	5.1 × 10 ²	1.6 × 10 ⁴	2.1 × 10 ²
TS: O(fcc), H(top)	-1	0.87/0.72	-0.49/-0.58	1.4 × 10 ⁵	2.6 × 10 ⁶	1.1 × 10 ⁶	4.7 × 10 ⁵
<i>H₂O(top) + O(fcc) → OH(fcc) + OH(bri)</i>	1	0.64/0.49	0.19/0.15	6.4 × 10 ⁵	1.6 × 10 ⁻³	2.1 × 10 ⁷	2.2 × 10 ⁻³
Fig. 9A to Fig. 9C	0	0.55/0.46	0.23/0.19	5.5 × 10 ⁶	7.0 × 10 ⁻⁴	2.0 × 10 ⁷	1.1 × 10 ⁻³
TS: OH(fcc), OH(top)	-1	0.67/0.60	0.47/0.45	3.3 × 10 ⁵	5.0 × 10 ⁻⁶	1.8 × 10 ⁶	1.8 × 10 ⁻⁶
Reaction on Ni(211)	F(V/ Å)	E _a /E _a ⁰ (eV)	$\Delta H_{\text{rxn}}/\Delta H_{\text{rxn}}^0$ (eV)	k _f (s ⁻¹) @ 463 K	K @ 463 K	k _f (s ⁻¹) @ 523 K	K @ 523 K
<i>H₂O(SLb) → OH(Sb) + H(Sb)</i>	1	1.14/0.94	-0.08/-0.25	2.5 × 10 ²	7.6 × 10 ²	4.0 × 10 ³	3.7 × 10 ²
Fig. 6A to Fig. 6D	0	0.99/0.81	-0.50/-0.63	5.5 × 10 ²	7.3 × 10 ⁵	4.8 × 10 ³	9.3 × 10 ⁴
TS: OH(Sb), H(St)	-1	0.71/0.52	-0.60/-0.74	1.8 × 10 ⁶	3.7 × 10 ⁷	7.7 × 10 ⁶	3.9 × 10 ⁶
<i>OH(Sb) + H(Sb) → OH(Sb) + H(SUh1)</i>	1	0.00/0.07	-0.14/-0.09	8.7 × 10 ¹¹	3.3	1.2 × 10 ¹²	2.4
	0	0.00/0.06	-0.14/-0.06	3.1 × 10 ¹⁵	1.8 × 10 ³	8.3 × 10 ¹⁵	2.9 × 10 ³
	-1	0.00/0.01	-0.12/-0.10	6.6 × 10 ¹²	20.4	7.6 × 10 ¹²	16.3
<i>OH(Sb2) → O(Sb) + H(SUh2)</i>	1	1.26/1.04	0.76/0.65	43.8	3.3 × 10 ⁻⁷	9.6 × 10 ²	2.4 × 10 ⁻⁶
Fig. 8A to Fig. 8C	0	1.07/0.86	0.49/0.37	8.8 × 10 ²	8.9 × 10 ⁻⁵	1.0 × 10 ⁴	2.5 × 10 ⁻⁴
TS: O(Sb), H(Sb)	-1	1.01/0.79	0.32/0.21	1.9 × 10 ⁴	3.6 × 10 ⁻³	2.0 × 10 ⁵	6.5 × 10 ⁻³

$O(Sb) + H(SUh2) \rightarrow O(SUh1) + H(ULh2)$	1	0.00/0.03	-0.34/-0.31	1.3×10^{13}	2.2×10^4	2.1×10^{13}	7.5×10^3
Fig. 8C to Fig. 8D	0	0.00/0.00	-0.25/-0.26	3.3×10^{12}	9.6×10^2	3.3×10^{12}	4.6×10^2
	-1	0.01/0.00	-0.15/-0.16	1.6×10^{13}	3.2×10^2	1.8×10^{13}	2.2×10^2
$O(SUh1) + H(ULh2) \rightarrow O(SUh1) + H(S4)$	1	0.26/0.21	-0.05/-0.09	1.1×10^{11}	1.9	2.1×10^{11}	1.4
Fig. 8D to Fig. 8F	0	0.27/0.21	-0.04/-0.09	3.1×10^9	0.9	5.0×10^9	0.6
TS: O(SUh1), H(Lt)	-1	0.28/0.24	-0.04/-0.07	5.4×10^{11}	2.1×10^3	1.3×10^{12}	2.0×10^3
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$H_2O(Sr) + O(SUh1) \rightarrow H_2O(Sr) + O(Sb)$	1	0.26/0.29	0.26/0.28	1.4×10^9	1.4×10^{-4}	3.3×10^9	2.7×10^{-5}
Fig. 10A to Fig. 10C	0	0.17/0.16	0.15/0.13	7.5×10^{10}	5.3×10^{-2}	1.2×10^{11}	7.2×10^{-2}
TS: OH(SUh1), OH(Lt)	-1	0.15/0.18	0.13/0.13	5.2×10^{11}	9.5×10^{-3}	1.1×10^{11}	1.2×10^{-2}
$H_2O(Sr) + O(Sb) \rightarrow OH(Sb2) + OH(Sb1)$	1	0.73/0.55	-0.41/-0.42	3.8×10^6	4.8×10^3	1.9×10^7	1.2×10^3
Fig. 10A to Fig. 10C	0	0.48/0.33	-0.56/-0.57	1.1×10^7	5.7×10^4	2.4×10^7	9.4×10^3
TS: OH(SUh1), OH(Lt)	-1	0.37/0.27	-0.56/-0.54	3.4×10^{10}	8.2×10^5	9.0×10^{10}	1.8×10^5
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Fig. 1. Part (a) and (b) show the top and side views of the initial adsorption configurations of the isolated H₂O, OH, and O species on a Ni (111) surface. The Ni, O, and H atoms are white, red, and purple respectively. Part (c) and (d) show the top and side views of a Ni (211) surface. The Upper-terrace and Step-edge Ni atoms are highlighted using a blue and green color, respectively.

Fig. 2. The electric field effects on the adsorption structures of an isolated H_2O molecule on a Ni(111) surface (a) and a Ni(211) surface (b). The electric field effects on the H_2O adsorption with a pre-adsorbed O atom on both the Ni(111) surface (c) and the Ni(211) surface (d). The differential charge densities of a H_2O molecule on Ni(111) and Ni(211) with and without electric fields are given in Part (e) and Part (f). The isosurface level of the differential charge densities is $0.003 \text{ electrons/Bohr}^3$, and the yellow or blue areas represent a gain or loss of electron, respectively. Number 1, 2, and 3 in the parenthesis corresponds to a the system with a negative electric field, with no fields, and with a positive field, respectively.

Fig. 3. The electric field effects on the adsorption energy of an isolated H₂O molecule (a), a H₂O molecule adsorbed with a pre-adsorbed O atom (b), a OH molecule (c), and an O atom (d) at their most favorable sites on a Ni(111) surface (dashed line) and a Ni(211) surface (solid line).

Fig. 4. Electric field effects on the reaction energy, ΔH_{rxn} , for the co-adsorption configurations of OH and H (A), O and H (B), and two OH molecules (C). The representations of line type refer to Fig. 3.

Fig. 5. The electric field effects on the $H_2O \rightarrow OH + H$ reaction pathway on Ni(111). The corresponding structures pertaining to the reaction pathways are presented as well. Since the structures (A~C) are significantly influenced by an external electric field, we also present their top and side views with and without electric fields. Fig. 5A1 to Fig. 5C1, Fig. 5A2 to Fig. 5C2, Fig. 5A3 to Fig. 5C3 represent the images with a positive field, no field, and a negative field, respectively. The energy scale refers to the H_2O adsorption energy on Ni(111) without a field.

Fig. 6. The minimum energy pathway of the $H_2O(SLb) \rightarrow OH(Sb2) + H(SUh1)$ reaction with an external electric field. All the energies refer to the adsorption of a H_2O molecule at a SLb site on Ni(211) with no fields. The energy scale refers to the H_2O adsorption energy on Ni(211) without a field.

Fig. 7. The minimum energy pathway of the $OH \rightarrow O + H$ reaction with and without an external electric field. The corresponding structures show the IS, TS, and FS without fields. All the energies refer to the adsorption energy of the OH species without an external electric field. The energy scale refers to the OH adsorption energy on Ni(111) without a field.

Fig. 8. The electric field effects on the $OH \rightarrow O + H$ reaction pathway on Ni(211). The corresponding structures show the initial, transition and final states in the absence of a field. The energy scale refers to the OH adsorption energy on Ni(211) without a field.

Fig. 9. Minimum energy pathway of the water dehydrogenation mechanism with a pre-adsorbed O atom on Ni(111) in the presence and absence of an external electric field. All the energies refer to the E_{ad} of a H_2O molecule with a pre-adsorbed O atom on Ni(111) without fields.

Fig. 10. Minimum energy pathway of the water dehydrogenation mechanism with a pre-adsorbed O atom on Ni(211) in the presence and absence of an external electric field. All the energies refer to the E_{ad} value of a H_2O molecule with a pre-adsorbed O atom on Ni(211) in the absence of a field.

Fig. 11. Energy profiles of water dehydrogenation on Ni(111) and Ni(211) with and without an external electric field. The $H_2O \rightarrow OH + H \rightarrow O + 2H$ and the $H_2O + O \rightarrow 2OH \rightarrow 2O + 2H$ reactions are mechanism 1 and mechanism 2 respectively. Part (a) and (b) show mechanism 1 and 2 on Ni(111) and Ni(211) without electric fields. The electric field effects on mechanism 1 and 2 on both Ni surfaces are given in Part (c) and Part (d). The energy scale of mechanism 1 and mechanism 2 refer to the E_a value of a H_2O molecule in the absence and presence of a pre-adsorbed O atom.

Fig. 12. Surface coverage of H₂O and OH species estimated from X-ray photoelectron spectroscopy (XPS) analysis of post-reaction Ni surface (a) and water consumption rates during MSR processes over Ni catalysts (b) with different electric fields. The XPS instrument was calibrated using both the Au 4f7/2 peak at 84.0 eV and the Ag 3d5/2 peak at 368.3 eV. XPS spectra for each of the samples were deconvoluted using CasaXPS to quantify individual oxygen species on the surface. Based on this deconvolution process, the surface coverage of H₂O and OH over the Ni surfaces was estimated.