Thesis for the degree of Doctor of Philosophy

Computational studies of nickel catalysed reactions relevant for hydrocarbon gasification

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Abstract

Sustainable energy sources are of great importance, and will become even more important in the future. Gasification of biomass is an important process for utilization of biomass, as a renewable energy carrier, to produce fuels and chemicals. Density functional theory (DFT) calculations were used to investigate i) the effect of co-adsorption of water and CO on the Ni(111) catalysed water splitting reaction, ii) water adsorption and dissociation on Ni(111), Ni(100) and Ni(110) surfaces, as well as iii) formyl oxidation and dissociation, iv) hydrocarbon combustion and synthesis, and v) the water gas shift (WGS) reaction on these surfaces.

The results show that the structures of an adsorbed water molecule and its splitting transition state are significantly changed by co-adsorption of a CO molecule on the Ni(111) surface. This leads to less exothermic reaction energy and larger activation barrier in the presence of CO which means that far fewer water molecules will dissociate in the presence of CO.

For the adsorption and dissociation of water on different Ni surfaces, the binding energies for H$_2$O and OH decrease in the order Ni(110) > Ni(100) > Ni(111), and the binding energies for O and H atoms decrease in the order Ni(100) > Ni(111) > Ni(110). In total, the complete water dissociation reaction rate decreases in the order Ni(110) > Ni(100) > Ni(111).

The reaction rates for both formyl dissociation to CH + O and to CO + H decrease in the order Ni(110) > Ni(111) > Ni(100). However, the dissociation to CO + H is kinetically favoured. The oxidation of formyl has the lowest activation energy on the Ni(111) surface.

For combustion and synthesis of hydrocarbons, the Ni(110) surface shows a better catalytic activity for hydrocarbon combustion compared to the other surfaces. Calculations show that Ni is a better catalyst for the combustion reaction compared to the hydrocarbon synthesis, where the reaction rate constants are small.

It was found that the WGS reaction occurs mainly via the direct pathway with the CO + O → CO$_2$ reaction as the rate limiting step on all three surfaces. The activation barrier obtained for this rate limiting step decreases in the order Ni(110) > Ni(111) > Ni(100). Thus, the WGS reaction is fastest on the Ni(100) surface if O species are present on the surfaces. However, the barrier for desorption of water (as the source of the O species) is lower than its dissociation reaction on the Ni(111) and Ni(100) surfaces, but not on the Ni(110) surface. Therefore the direct pathway on the Ni(110) surface will dominate and will be the rate limiting step at low H$_2$O(g) pressures. The calculations also reveal that the WGS reaction does not primarily occur via the formate pathway, since this species is a stable intermediate on all surfaces.

All reactions studied in this work support the Brønsted-Evans-Polanyi (BEP) principles.

Keywords: DFT, H$_2$O, CO, adsorption, dissociation, formyl, hydrocarbon combustion, hydrocarbon synthesis, water gas shift, gasification, Ni(111), Ni(110) and Ni(100)
List of Publications

This thesis is mainly based on the results presented in the following publications:


Paper II: **A. Mohsenzadeh**, K. Bolton, T. Richards, *DFT study of the adsorption and dissociation of water on Ni (111), Ni (110) and Ni (100) surfaces*, Surface Science, 627 (2014) 1-10.


Paper V: **A. Mohsenzadeh**, T. Richards, K. Bolton, *DFT study of the water gas shift reaction on Ni(111), Ni(100) and Ni(110) surfaces*, In press.

Statement of Contribution

Paper I: Performed all the calculations and responsible for the data analyses and writing the manuscript and its revision.

Paper II: Performed all the calculations and responsible for the data analyses and writing the manuscript and its revision.

Paper III: Performed all the calculations and responsible for the data analyses and writing the manuscript and its revision.

Paper IV: Performed all the calculations and responsible for the data analyses and writing the manuscript and its revision.

Paper V: Performed all the calculations and responsible for the data analyses and writing the manuscript and its revision.
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## CONCLUSIONS

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The emission of greenhouse gases such as CO₂ is one of the main reasons for climate changes [1, 2]. It is therefore important to move to a carbon-neutral fuel economy, and one route towards such an economy is the conversion of biomass into fuels [3]. Biomass, which is generated from CO₂ and H₂O by photosynthesis, can thereby be converted into fuels that are again combusted to H₂O and CO₂. In this scheme, energy is extracted from sunlight, through a short period carbon cycle, without release of carbon from fossil fuel reserves. Four of the six steps in the carbon cycle, labelled as 1-4 in the Figure 1.1, use heterogeneous catalysis. Understanding the mechanisms of these catalytic processes is needed to improve their efficiency and to identify optimal catalysts and operating conditions.

The density functional theory (DFT) can be used to understand the ionic and electronic structure of atomic complexes and surface structures and consequently reactions occurring in
heterogeneous catalysis. The DFT is a reliable tool for studying chemical reactions, providing adsorption energies and reaction barriers as well as minimum energy paths on the potential energy surface connecting reactant(s), transition state(s), and product(s). The output of DFT calculations can be coupled to properties at the mesoscopic level via ab initio thermodynamics, and in particular, kinetic modelling.

There are some limitations with DFT method. The band-gaps in semiconductors and insulators are underestimated, whereas, the lattice constants, cohesive energies, and bulk moduli are overestimated [4, 5]. Also, the strong correlations and van-der-Waals interactions are neglected in traditional DFT methods. It also may be noted that, compared to many other techniques such as force fields, the DFT is costly in terms of computer resources. However, this method has been shown to give impressive results [5], and is widely used to study the trends of heterogeneous catalytic reactions [6-14].

1.1 Background

Gasification of biomass is an important process for utilization of biomass, as a renewable energy carrier, to produce fuels and chemicals. In fact, the gasification process involves the partial combustion of biomass to produce gaseous fuels (which are often referred to as synthesis gas or syngas) by heating in a gasification medium such as steam, oxygen or air. The gaseous products can be used for generation of heat or electricity, synthesis of liquid transportation fuels, production of hydrogen fuel, synthesis of chemicals, manufacturing of fuel cells, etc. [15].

The water gas shift (WGS) reaction, \( CO + H_2O \rightleftharpoons CO_2 + H_2 \), is one of the main reactions during gasification process [16] and several other industrial processes, such as steam reforming of natural gas, methanation and production of hydrogen for use in, e.g., fuel cells [17]. Different catalysts are used to increase the efficiency of this reaction, e.g., nickel which is widely applied due to its high heat conductivity, high catalytic conversion and the capability of being manufactured in different shapes [6, 17-20]. Recent investigations suggest that the reaction mainly occurs via three possible mechanisms including the direct, carboxyl, and formate pathways [6, 14, 21, 22]. It is believed that dissociation of water is one of the rate determining steps of the WGS reaction [23]. The interaction of water with solid surfaces is of great importance in many other physical, chemical and biological processes, e.g., steam methane reforming (SMR) [14, 24] where nickel is frequently used as the catalyst.

Also, the formate (HCOO) species is an intermediate that has the highest concentration in the WGS reaction [25-27] and is central in the formate mechanism, where oxidation of CHO is one of the possible routes of its formation (CHO + O \rightleftharpoons HCOO).
For a more complete understanding of heterogeneous catalysis, it is essential to account for the effect of co-adsorption of reactive chemical species on catalyst surfaces. A typical species can be co-adsorbed is CO, which plays a key role in many catalytic reactions, e.g., the oxidation of carbon monoxide and CO methanation [28-35].

Another important technology which has been developed for efficient energy production with minimum pollutant formation is catalytic combustion of hydrocarbons. Compared to conventional flame combustion, catalytic combustion is used at lower temperatures, and the catalyst plays a decisive role in the improvement of this process [36-38]. A conclusion drawn from earlier studies [39, 40] was that the combustion process proceeds via dissociation of the hydrocarbon into hydrogen and carbon followed by oxidation reactions. However, recent studies suggest that the direct reaction between oxygen and CH fragments can be the most important pathway where an oxymethylidyne (CHO, formyl) intermediate is formed and then dissociates to carbon monoxide and hydrogen [41, 42].

The synthesis of hydrocarbons from syngas is probably the most important method for production of fuels and chemicals using non-petroleum based sources since the early developmental work by Fischer and Tropsch and their co-workers [43]. In the Fischer-Tropsch synthesis (FTS) process, the synthesis gas is converted into various hydrocarbons and water over catalysts such as transition metals [44, 45]. These hydrocarbons can be used as fuel or as feedstock in the chemical industry. The FTS has been investigated both theoretically [42, 46, 47] and experimentally [48-50]. Recent investigations reveal that the reaction via CHO intermediate is the main reaction pathway [51-54]. However, previous studies suggested that both CO and H₂ adsorb on the catalyst surface and subsequently dissociate. Then both carbon and oxygen are hydrogenated to CH₂ and H₂O [55].

Previous studies indicate that the catalytic properties and reaction energies are affected by surface orientation, steps and defects [56-58]. The particles of nickel can grow on oxide or graphite substrates and have polyhedral shapes exhibiting (111), (100) and (110) facets [59].

1.2 Objectives

The objective of this study is to investigate the effect of crystallographic structure of the nickel catalyst on several heterogeneous catalysis processes including the water dissociation, the formyl oxidation and dissociation, the hydrocarbon combustion and synthesis and the WGS reaction. For this purpose, the DFT simulation tools were employed to investigate the energetics, and to optimize the geometrical structures of intermediates in the catalytic surface reactions discussed in the previous section. The same methods and models are used for all surfaces and reactions to elucidate how the reactant, transition state or product relative energies or vibrational frequencies are affected by the crystallographic structure of the nickel
catalyst. These data can be used to model the kinetics of the process, to bridge a direct connection between macroscopic observations in experiments and microscopic understanding from computations, and to design novel catalysts for these processes.

1.3 Outline of the thesis

This thesis focuses on water splitting on a Ni(111) surface in the absence and presence of a co-adsorbed CO molecule (paper I), as well as comparative DFT studies of the water adsorption and dissociation (paper II), formyl oxidation and dissociation (paper III), the hydrocarbon combustion and synthesis (paper IV) and WGS reaction (paper V) on the Ni(111), Ni(100) and Ni(110) surfaces to postulate potential pathways for these reactions.
The electronic structure reflects the spatial and energetic distribution of electrons of an atom, a molecule or a piece of bulk material. The density functional theory (DFT) provides a framework to obtain the electronic structure and the total energy using the concepts of quantum mechanics [60, 61], and therefore can be employed to find stable geometries, calculate binding energies, magnetic, and electronic properties etc. The DFT can be used to address a vast variety of systems and problems in physics, chemistry, biology, and materials science. In this section, a brief summary of the fundamental points of the DFT formalism is provided focusing on a particular scheme, i.e., where the formulation of plane-waves (PWs) in combination with pseudopotentials (PPs) are considered [61].

2.1 The many-body problem

We need to solve time-independent Schrödinger equation (which is a second order, partial differential equation, and it is written here in the eigenvalue form) for studying and analysing the stationary properties of matter:

\[
H_{tot} \Psi_{tot}(\mathbf{R}, \mathbf{r}) = E_{tot} \Psi_{tot}(\mathbf{R}, \mathbf{r})
\]  

(2.1)

where \(H_{tot}\) is the total Hamiltonian, \(\Psi_{tot}\) is the total many-body wavefunction, and \(E_{tot}\) is the total energy of the system. \(\Psi\) are eigenfunctions with the corresponding energy eigenvalues \(E\), and the lowest energy eigenvalue is referred to as the ground-state energy of the system \((E_0)\).
All energies higher than the ground-state energy are excited states, and physical and chemical properties of a system can be determined if $\Psi$ and $E$ are known.

Since the mass of the nucleus is much larger compared to the electron (at least three orders of magnitude), the electronic and nuclear degrees of freedom can be separated. This gives a many-body wavefunction in a separable form as

$$\Psi_{tot}(R, r) = \Psi_e(R, r) \lambda(R)$$  (2.2)

where $\Psi_e(R, r)$ is the electronic part and $\lambda(R)$ is the nuclear part. This approach is referred to as the Born-Oppenheimer (BO) approximation [62]. Thus, the problem is simplified to the time-independent, non-relativistic Schrödinger equation (note that the atomic units are used in Equation 2.3, i.e., $\hbar = \frac{1}{4\pi\varepsilon_0} = m_e = e = 1$):

$$H_e \Psi_e(r_i) = E_e \Psi_e(r_i)$$  (2.3)

where

$$H_e = T_e + V_{ne} + V_{ee} + V_{nn}$$  (2.4)

and

$$T_e = -\frac{1}{2} \sum_i^N \nabla_i^2$$  (2.5)
$$V_{ne} = -\sum_a^N \sum_i^N \frac{Z_a}{|R_a - r_i|}$$  (2.6)
$$V_{ee} = \sum_i^N \sum_{j > i}^N \frac{1}{|r_i - r_j|}$$  (2.7)
$$V_{nn} = \sum_a^N \sum_{b > a}^N \frac{Z_a Z_b}{|R_a - R_b|}$$  (2.8)

where $T_e$ is the kinetic energy, $V_{ne}$ is the electron-nuclei Coulomb potential, $V_{ee}$ is the electron-electron Coulomb potential, and $V_{nn}$ is the nuclei-nuclei Coulomb potential. $Z_a$ is the atomic number of nucleus $a$, $R$ and $r$ denote nuclear and electronic coordinates, and $\nabla_i^2$ is the Laplace operator of particle $i$ given as

$$\nabla_i^2 = \left( \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2} \right)$$  (2.9)

The potential that the nuclei move in is obtained by solving the electron density. Therefore, the total groundstate energy can be expressed as a function of the coordinates of nuclei which yields the potential energy surface (PES).

It may be noted that even within the BO-approximation, it is still hard to solve the electronic problem for systems with more than one electron.
One approach to solve the electronic problem is the Hartree-Fock approach which is based on approximations of the electronic many-body wavefunction [63-67]. Another approach, suggested by Thomas [68] and Fermi [69], is to use the electron density, \( n(r) \), instead of the many-body wavefunction. In their model the problem for a system of \( N \) interacting electrons is reduced to only 3 dimensions.

### 2.2 The density functional formalism

For a system of \( N \) electrons, solutions for Equations 2.3-2.8 can be utilized to construct an electron density \( n(r) \), which implies that \( n(r) \) is determined by the external potential. Two theorems developed by Hohenberg and Kohn [60] state that the opposite is also true. The total energy of a system is a unique functional of the electronic density (to an additive constant), and therefore the ground-state energy \( (E_0) \) is known by knowing the ground-state density \( (n_0) \). This can be written as

\[
E[n] = \int v_{\text{ext}}(r)n(r)dr + F[n] \tag{2.10}
\]

and

\[
E_0[n_0] = \int v_{\text{ext}}(r)n_0(r)dr + F[n_0] \tag{2.11}
\]

and

\[
F[n] = T_e[n] + V_{ee}[n] \tag{2.12}
\]

where \( F[n] \) is a universal functional with no dependence on the external potential and contains the kinetic and the Coulomb energies of the system. Hence, the ground-state energy is obtained through a minimization problem as

\[
E_0 = \min E[n(r)] = E[n_0(r)] \tag{2.13}
\]

Kohn and Sham [70] developed a method to calculate \( n_0 \) and \( E_0 \) within the DFT formalism, which presently is used in most DFT implementation. They constructed an effective potential \( (v_{\text{eff}}) \) for a fictitious system (referred to as a KS system) of non-interacting electrons to calculate an electron density which is identical to that of the real system of interacting electrons. The universal functional for \( F[n] \) can be expressed as

\[
F[n] = \tilde{T}_e[n(r)] + \frac{1}{2} \int \frac{n(r)}{|r-r'|} dr + E_{xc}[n(r)] \tag{2.14}
\]

where the first term, \( \tilde{T}_e \), is the kinetic energy of the non-interacting system with a density \( n(r) \), the second term contains the classical, direct Coulomb energy (also referred to as the Hartree energy), and the last term is the exchange-correlation energy, \( E_{xc} \), which collects the
The difference in kinetic energy between the real (interacting) and fictitious (non-interacting) systems ($\tilde{T}_e - T_e$) as well as the non-direct electron-electron interaction; exchange and correlation. Each electron in the system is interacting to itself since the Coulomb term includes the density of all electrons. This self-interaction is cancelled due to the exact treatment of exchange in a Hartree-Fock formulation. In density functional theory, however, these contributions are cancelled if the true form of the exchange-correlation potential is known. Consequently, it is critical in DFT to approximate the exchange-correlation potential since the exact form, which includes all the many-body effects, is unknown. The exchange-correlation potential is defined as

$$V_{xc} = \frac{\delta E_{xc}[n]}{\delta n(r)}$$  \hspace{1cm} (2.15)$$

The local density approximation (LDA) approach was suggested Kohn and Sham [70] where the inhomogeneous system is considered as locally homogeneous. Therefore, the local terms are calculated by an integral over the exchange-correlation energy per electron ($\epsilon_{xc}$) as

$$E_{xc}^{LDA}[n] = \int n(r)\epsilon_{xc}[n(r)]dr$$  \hspace{1cm} (2.16)$$

The constructed density decays in an asymptotic exponential manner which causes many of the problems related to the LDA approximation such as overestimation of the dissociation energies of molecules. An improved method beyond the LDA is the generalized gradient approximation (GGA) [71, 72] which includes density gradients in addition to the local electron density as

$$E_{xc}^{GGA}[n] = \int n(r)\epsilon_{xc}[n(r),\nabla n(r)]dr$$  \hspace{1cm} (2.17)$$

A number of functionals have been developed based on the GGA approach including Perdew-Wang-91 (PW91) [73], Perdew-Burke-Ernzerhof (PBE) [74], revised PBE [75], and RPBE [76]. Although, the behaviour and the accuracy of functionals should be evaluated for each situation, the GGA functionals generally give results that are in better agreement with experimental chemisorption, binding and atomic energies, and bond lengths and angles compared to LDA [76, 77]. It may be noted that there is a limit for the accuracy of the GGAs due to the exchange term, the inadequate description of the non-local contributions, and presence of self-interaction in the Hartree term. In addition to LDA and GGA functionals, there are other functionals that use higher levels of theory at the expense of increased computational costs, e.g., the meta-GGA and hybrid functionals which include higher order derivatives of the density change and combine the exact exchange from a Hartree-Fock theory with correlation energy calculated from, e.g., GGA calculations. PBE0 [78] and B3LYP [79] are the most common hybrid functionals within DFT.

The minimization problem suggested by Hohenberg and Kohn leads to a set of KS-equations that can be solved for the KS-orbital under the constraint that the total number of electrons is conserved. This can be written as

$$\left[-\frac{1}{2}\nabla^2 + u_{eff}(r)\right]\phi_i(r) = \epsilon_i\phi_i(r)$$  \hspace{1cm} (2.18)$$
Here, $\epsilon_i$ is the orbital energy of the corresponding KS-orbital, $\phi_i(r)$, and

$$v_{\text{eff}}(r) = v_{\text{ext}}(r) + v_H(r) + v_{xc}(r)$$ (2.19)

where $v_{\text{ext}}$ is the external potential acting on the interacting system, $v_H$ is the Hartree (or Coulomb) potential, and $v_{xc}$ is the exchange-correlation potential.

The density is calculated as

$$n(r) = \sum_{i=1}^{N} \phi_i^*(r)\phi_i(r)$$ (2.20)

where $N$ is the number of electrons and $\phi_i(r)$ is the KS-orbital.

It may be noted that the energy eigenvalues ($\epsilon_i$) are a consequence of the applied variational principle and appear as Lagrange multipliers, and therefore they have no obvious physical meaning. The KS-orbitals, $\phi_i(r)$, are constructed to satisfy Equation 2.18 and to provide the correct electron density. They also have no clear physical meaning. In practice, however, $\epsilon_i$ and $\phi_i(r)$, can be used to draw qualitative conclusions. The sum of $\epsilon_i$ is a large part of the total energy, and KS-orbitals are associated with the electron density.

The exchange correlation and the Hartree potentials need to be evaluated for solving the one-electron KS-equations (Equation 2.18) at the same time that they are a function of the electron density. The density is obtained by the KS-orbitals which in turn are given by solving the KS-equations. Therefore, an iterative approach is applied where a set of trial orbitals, $\{\phi_i\}_j$, is used to construct the initial density. Then, the KS-equations are solved for a new set $\{\phi_i\}_{j+1}$. The solution (which consequently is the ground-state density) has been found if the new and the old sets are consistent. In practice, a combination of new and old densities is used for the iterations until the calculated orbitals do not vary from one cycle to another. This is referred to as the self-consistent field (SCF) loop.

2.3 The plane-wave basis

The choice of the expansion functions for KS-orbitals [$\phi(r)$] is of great importance in the application of DFT. The plane-wave (PW) method originates from calculations of extended bulk and surface systems. According to the Bloch's theorem, the KS-orbitals can be written as a product of a periodic cell and a wave-like part as

$$\phi_j(r) = e^{i\mathbf{k} \cdot \mathbf{r}}u_j(r)$$ (2.21)

where $\mathbf{k}$ is a point in Brillouin zone, $u_j(r)$ is a function which has the same periodicity as the cell, and $e^{i\mathbf{k} \cdot \mathbf{r}}$ is a plane wave. The periodic cell contribution can be expressed as a sum using a basis set of plane-waves as
\[ u_j(\mathbf{r}) = \sum G c_{j,G} e^{iG \cdot \mathbf{r}} \] (2.22)

where \( c_{j,G} \) are expansion coefficients and \( G \) are the reciprocal lattice vectors defined as
\[ G \cdot a = 2\pi n \] (2.23)

where \( a \) are the real space lattice vectors and \( n \) is an integer.

The final expression of the KS-orbitals, where each electronic wavefunction is expressed as a sum of plane-waves, can be written as
\[ \phi_j(\mathbf{r}) = \sum c_{j,k+G} e^{i(k+G) \cdot \mathbf{r}} \] (2.24)

The summation is applied over all wave vectors (\( G \)). The expansion coefficients (\( c_{j,G} \)), in practice, decrease by increasing \( |k+G| \), which implies that a reduced set of plane-wave expansion terms must be considered: \( |k+G|^2 \leq 2E_{cut} \). This is a simple way to control the computational accuracy since the basis set size varies accordingly together with the accuracy by setting the cut-off energy, \( E_{cut} \).

Plane wave basis set is complete and unbiased and is not dependent on atomic positions. However, the number of plane waves needed is quite large. Also, the size of basis set increases with increasing the box size, i.e., the vacuum region is included in the calculations which considerably affects the computational costs [80].

### 2.4 Pseudopotentials

Many of the physical and chemical properties of molecules and solids are derived due to the interactions between the valence electrons. The core electrons do not directly contribute to bonding properties, and are not affected by changes in bonding. These electrons are important due to screening of the nucleus charge and forming an effective potential for the valence states. Therefore, the interactions between the core and the valance electrons can be replaced by a weaker fictitious potential which is referred to as a pseudopotential (PP). It is difficult to describe the rapid oscillations of core and valence states in the core region, and therefore using pseudopotentials leads to a highly reduced basis set.

The effect of the nucleus and core electrons on the valance states are modelled by potentials as
\[ V^{PP}(\mathbf{r}) = v_L^{PP}(\mathbf{r}) + \sum_i v_{NL}^{PP}(\mathbf{r}) \hat{P}_i \] (2.25)
where the first term, $u_L^{PP}(\mathbf{r})$, is the local part and the second term, the non-local part, accounts for orthogonality between the valence and core states. $P_l$ is the projection operator used to project out the different angular components of the wave function.

Several conditions should be fulfilled to construct pseudopotentials. The charge which is integrated within a cut-off radius ($r_c$) should agree between the all-electron (AE) and pseudo-descriptions. This is referred to as norm-conservation. In addition, the calculations using pseudopotentials should provide the same KS-eigenvalues ($\epsilon_i$) as all electron calculations. It may be noted that choosing a suitable pseudization radius, that will not affect the valence states and consequently the chemical bonding, is of great importance. A larger basis is needed for a smaller radius, i.e., a larger cut-off or more plane-waves. This is referred to as hardness.

It is expected that the same pseudopotential can be transferred between different chemical environments and still reproduce accurate results, which is referred to as transferability of pseudopotentials. However, the idea that the same potential is able to describe different configurations turns out to be questionable sometimes since the pseudopotentials are generated with a specific electronic configuration. Norm-conserving [81] and ultrasoft [82] potentials are the most commonly used potentials. Ultrasoft pseudopotentials (UPPs) have often better transferability and the norm-conservation conditions are "softer" for them. Thus a smaller number of basis functions are needed and therefore smaller cut-offs, which considerably reduces computational costs. In may be noted that UPPs are more difficult to construct.

The projector augmented wave (PAW) method, introduced by Peter Blöchl in 1994 [83], is a generalization of the pseudopotential and linear augmented plane wave (LAPW) methods. The LAPW basis is constructed by dividing the unit cell into spheres around each atom, where the wavefunctions are atomic-like and oscillate rapidly, and the remaining region, where the wavefunctions are not atomic-like and smoothly vary. Each basis function is then defined as a linear combination of atomic-like functions in the spheres connected to a plane wave in the interstitial region. Similarly, the PAW method addresses the rapidly oscillating wavefunctions near the core into smooth wavefunctions which allows for DFT calculations to be performed with greater computational efficiency. Generally, the accuracy of PAW method is improved compared to the UPPs and generation of datasets is easier than for UPPs. In the presented study, the PAW method has been applied for all the calculations.

2.5 Integration over the Brillouin zone

The calculations of the total energy involve integrals over the Brillouin zone. Among the suggested approximations that allow one to consider a reduced set of k-points and to replace the integration with a summation, a $4\times4\times1$ Monkhorst-Pack scheme [84] has been applied in
the present study for the numerical integration in reciprocal space. It worth to mention that the size of the k-mesh used depends on the size of the computational cell and the type of the material which is investigated. Smaller Brillouin zone (BZ) sampling intervals (5×5×1 and 6×6×1) were tested and showed insignificant differences in the energies of the optimized structures (less than 0.01 eV).
CHAPTER 3

MODELING MATERIALS PROPERTIES

3.1 Slab model

Computational resources available for simulations are limited and consequently modelling all the atoms in a large particle is not possible. A strategy is therefore required in order to reduce the size of the system. A slab approach has been selected for the calculations in the present study, in order to describe surfaces with periodic structure in the surface plane. This is shown in Figure 3.1. The dashed lines represent the computational cell, often referred to as a supercell, which is repeated in the three directions to model an infinite two dimensional surface.

The corresponding bulk material is truncated in the desired crystallographic direction in order to construct the surface slab model. Truncating the bulk affects the electronic structure. Thus the slab thickness needs to be large enough to retain this effect, where the bottom layers of the slab are fixed in their bulk positions to provide a representative model of the semi-infinite bulk material.

Also, a large enough volume of vacuum in the surface perpendicular direction (z-direction) is needed to avoid the interaction between atoms on the surface and the neighbouring cell (see Figure 3.1).

It may be noted that the results of calculations, e.g., adsorption energies, are affected by the coverage due to the electrostatics between adsorbates in neighbouring computational cells.
In **Paper I**, a Ni(111) surface model with $4 \times 4$ unit cell was used containing five atomic layers that were separated by an equivalent volume of vacuum in the surface perpendicular direction. The two bottom layers of the slab were fixed to maintain the bulk crystal structure, and the three upper layers were free to relax. This slab size was selected to avoid the interactions between the adsorbates and neighbouring images since there were water and carbon dioxide co-adsorbed on the surface. In **Papers II-V**, a four-layer slab with a $2 \times 2$ unit cell was used to model the Ni surfaces. The two bottom layers of the slab were fixed and the two upper layers were free to relax. This unit cell size yields converged results in a computationally feasible time and is commonly used in investigations of similar systems [6, 85, 86].

### 3.2 Adsorption sites

As shown in the **Figure 3.2**, there are four high symmetry adsorption sites on the Ni(111) crystal surface. A top site is above the uppermost Ni surface atom and is labelled A, the hcp
3-fold hollow site is labelled C, the fcc 3-fold hollow site is labelled C' and the 2-fold bridge site between two neighbouring atoms is labelled B. In addition to the top and bridge sites labelled A and B, the Ni(100) crystal surface has a square 4-fold hollow adsorption site labelled D'. There are five high symmetry adsorption sites on the Ni(110) surface. These are the top site labelled A, a 2-fold long bridge site labelled E, a 2-fold short bridge site labelled F, a rectangular 4-fold hollow site labelled D and a quasi 3-fold hollow site labelled G.

![Figure 3.2 Different adsorption sites on the Ni(111), Ni(100) and Ni(110) surfaces. A is a top site; B is a bridge site; C is a hcp site; C' is a fcc site; D is a rectangular 4-fold hollow site; D' is a square 4-fold hollow site; E is a long bridge site; F is a short bridge site; G is a pseudo 3-fold hollow site.](image)

### 3.3 The potential energy surface and vibrational frequencies

The potential experienced by the nuclei is obtained by solving the electronic problem. Optimizations are generally done by evaluating the forces (\( \mathbf{F} \)) acting on the ions, i.e., the derivative of the energy with respect to the position of the atoms (\( R_i \)) as

\[
\mathbf{F} = -\nabla R_i E_{tot}
\]

where \( \nabla \) is the gradient operator and \( E_{tot} \) is the total energy of the system.

Vibrational frequencies can be calculated from electronic structure calculations when \( \Delta \mathbf{F} = 0 \), i.e., at the stationary points on the potential energy surface. A second-derivative matrix of the energy, often referred to as the Hessian matrix \([87]\), can be constructed as
\[ H_{ij} = \frac{1}{\sqrt{m_i m_j}} \frac{\delta^2 E}{\delta q_i \delta q_j} \]  

(3.2)

where \( q_i \) and \( q_j \) are coordinates of atoms \( i \) and \( j \), with corresponding masses of \( m_i \) and \( m_j \). Finite differences are used to estimate the second order derivatives. The corresponding eigenvalues and eigenvectors, which are the vibrational frequencies and normal mode eigenvectors, are calculated by diagonalizing the Hessian matrix. The calculated vibrational frequencies can be used to confirm that the stationary structures are minimum energy (zero imaginary frequencies) or transition states (one imaginary frequency) and to calculate the vibrational partition functions and zero point vibrational energies (ZPVEs).

3.4 Adsorption energies

The system rearranges to minimize the total energy when an atom or molecule approaches the surface. The adsorption energy can therefore be calculated by looking at energies of two extreme systems, i.e., the relaxed and the non-interacting system. The adsorption energies (\( E_{\text{ads}} \)) of the reactants and products were calculated as

\[ E_{\text{ads}} = E_{\text{surf} + \text{adsorbate}} - E_{\text{surf}} - E_{\text{adsorbate}} \]  

(3.3)

where \( E_{\text{surf}} \) is the total energy of the geometry optimized surface, \( E_{\text{adsorbate}} \) is the total energy of the isolated, geometry optimized adsorbate(s) in the gas phase and \( E_{\text{surf} + \text{adsorbate}} \) is the total energy of the geometry optimized surface-adsorbate(s) system.

3.5 Transition states and activation barriers

Density functional theory has been successfully used to calculate transition states and activation barriers of chemical reactions [5]. This can be done by identifying a minimum energy path (MEP) on the potential energy surface (PES) that connects a reactant and a product structure. In a chemical reaction, the transition state is a particular configuration along the reaction coordinate which has the highest potential energy. Therefore, a first-order saddle point, between the reactant and the product structures, needs to be located on the PES. At this point, the curvature in all directions, except one, is positive. A schematic representation of a potential energy surface is shown in Figure 3.3.
The reactant needs to overcome an energy barrier, which is referred to as activation energy or barrier, as the reaction proceeds to product. It may be noted that both reactants and products are local minimums on the PES, and a specific reactant may lead to different products.

The climbing image-nudged elastic band (CI-NEB) method [88, 89] was used to locate the transition states, where the lowest energy reactant and product configurations are selected as the initial and final states. Then, six images are placed between the reactant and product geometries. In a regular NEB [90] method, the calculations are performed making use of a series of constrained optimizations between the reactant and product states. In contrast, in the CI-NEB method, the corresponding maximum-energy image does not feel the constraint imposed on the rest of the images, and therefore results in the true transition state.

The dimer approach [91] was also employed to locate some of the transition states using the same convergence criteria. In this method, the most stable configuration of the reactant on the surface is determined using a standard DFT minimization method before searching for a nearby saddle point.

As mentioned before, a frequency analysis is needed to validate the TS where the vibrational frequency calculation yields one imaginary frequency while the other frequencies are positive as a consequence of the gradient requirement on PES. The imaginary eigenvector was used to validate that the TS was correct for the desired reactant-products reaction path.

![Figure 3.3](image-url) A schematic representation of a potential energy surface (PES). The figure is inspired by Ref. [92].
3.6 Rate constants and reaction kinetics

The vibrational frequencies are also used to estimate the rate constants \( k \) from the transition state theory [93] as

\[
    k = \left( \frac{k_B T}{\hbar} \right) \frac{q}{q^\dagger} e^{-\frac{E_a}{k_B T}} \quad (3.4)
\]

where \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature and \( \hbar \) is Planck’s constant. \( q \) and \( q^\dagger \) are the partition functions for the reactant and the transition state, respectively, and \( E_a \) is the ZPVE corrected activation energy. The partition functions were calculated using harmonic vibrations. Although this approximation may affect the quantitative results presented in this study, it is not expected to affect the trends [13, 57, 85, 94, 95].

For the reaction kinetics, the ODE45 solver in the MATLAB R2013a simulation package [96] was employed to solve the related ordinary differential equations (ODEs) using the rate constants determined by the DFT calculations.

3.7 Density of states and charge density

Interpretation of the electronic structure aids the understanding of material properties and clarifying the results. The number of states per energy \( E \), normalized to the total number \( N \), is obtained by a direct projection of the state-density on the energy as

\[
    DOS = D(E) = \frac{1}{N} \sum_n \langle \phi_n | \phi_n \rangle \delta(E - E_n) \quad (3.5)
\]

where \( E_n \) are the eigenvalues of the KS eigenstates \( (\phi_n) \). A schematic representation of the density of states corresponding to a number states available within an energy interval is shown in Figure 3.4.

The projected density of states (PDOS) provides further resolution by considering contributions from different angular momenta as

\[
    PDOS = D_{lm}(E) = \frac{1}{N} \sum_n \langle \phi_n | \phi_{lm} \rangle \langle \phi_{lm} | \phi_n \rangle \delta(E - E_n) \quad (3.6)
\]

The charge density on each ion was calculated by integrating the valence charge density within the Wigner-Seitz spheres around each atom. The radius was selected such that the total volume over all atoms is approximately 100% and that the ratios of the atomic radii is equal to that of the ionic radii [97].
3.8 Brønsted-Evans-Polanyi principle and the transition state scaling method

These methods have been applied to validate the results of the calculations. The Brønsted-Evans-Polanyi (BEP) principle states that the activation energy for a given reaction should be linearly proportional to the reaction energy [98, 99]. The transition state scaling (TSS) method [100, 101] is often used interchangeably with the BEP relationship. This method correlates the energy of the transition state ($E_{TS}$) with the energy of either the initial state ($E_{IS}$) or final state ($E_{FS}$) of a reaction.
CHAPTER 4

SUMMARY OF THE APPENDED PAPERS

4.1 Paper I

Using DFT calculations, the effect of co-adsorption of carbon monoxide on the adsorption and dissociation of water on the Ni(111) surface has been studied. As discussed in Paper I, the geometry optimizations of the reactants and products were performed on the sites that have previously been shown [14] to yield the lowest energy structures, i.e., the most favourable sites. The results are shown in Table 4.1.

In the absence of CO, the water molecule (the reactant) is adsorbed on the top site (site A in Figure 3.2) via its O atom with an binding energy of −0.27 eV. Both of its O-H bonds have similar lengths. Both OH and H (the products) are adsorbed on the fcc site (site C′ in Figure 3.2) with an adsorption energy of −5.83 eV. The OH is adsorbed via the O atom similarly to the water molecule.

For co-adsorbed CO and H₂O, and for co-adsorbed CO, H and OH, the obtained energies are −2.32 eV and −7.63 eV, respectively. The presence of the CO does not affect the preferred adsorption sites. However the reactant geometry is affected by co-adsorbed CO. The O-H bonds in the single water molecule are almost the same whereas, in the presence of CO, the O-H bond closest to the CO molecule is 0.015 Å longer than the other bond. This is probably due to interactions between the CO molecule and this H atom since the distance between them is only 1.88 Å. These interactions are also reflected in the vibrational frequencies as the asymmetric stretching mode is lowered from 3612 cm⁻¹ to 3412 cm⁻¹ in the absence and
presence of CO, respectively. The products geometry or vibrational modes are not significantly affected by the presence of CO.

Table 4.1 Adsorption energies (eV) and structural parameters (Å) of reactants and products with and without co-adsorbed carbon monoxide.\(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption site</th>
<th>E(_{\text{ads}})</th>
<th>d(_{\text{surf-adsorbate}}) (^b)</th>
<th>Bond length (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>A</td>
<td>−0.27</td>
<td>H(_2)O: 2.157</td>
<td>O-H(_a): 0.979</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O-H(_b): 0.978</td>
</tr>
<tr>
<td>H(_2)O + CO</td>
<td>H(_2)O: A</td>
<td>−2.32</td>
<td>H(_2)O: 2.114 CO: 1.903</td>
<td>O-H(_a): 0.990</td>
</tr>
<tr>
<td></td>
<td>CO: C’</td>
<td></td>
<td></td>
<td>O-H(_b): 0.975</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C-O: 1.213</td>
</tr>
<tr>
<td>OH + H</td>
<td>OH: C’</td>
<td>−5.83</td>
<td>OH: 1.950 H: 1.655</td>
<td>O-H(_a): 0.973</td>
</tr>
<tr>
<td></td>
<td>H: C’</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH + H + CO</td>
<td>OH: C’</td>
<td>−7.63</td>
<td>OH: 1.923 H: 1.646 CO: 1.872</td>
<td>O-H(_a): 0.974</td>
</tr>
<tr>
<td></td>
<td>H: C’</td>
<td></td>
<td></td>
<td>O-C-O: 1.195</td>
</tr>
<tr>
<td></td>
<td>CO: C’</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Adsorption energies are ZPVE-corrected values. \(^b\) Shortest distance between any atom of the adsorbate(s) and any metal atom on the surface. \(^c\) Letter “a” shows the O-H bond nearest the CO and “b” the other O-H bond.

The distances between the surface and both reactants and products are decreased when the CO is present. The reason is probably the electron transfer from the CO to the surface. The total charge density on the uppermost Ni atoms is higher in the presence of CO than in the absence of CO. Hence, the interaction strengths between the surface and the adsorbates increases, which is also seen by an increase in the charge density of adsorbates.

Figure 4.1 shows the water splitting reaction coordinates with and without co-adsorbed CO. The length and frequency of the breaking bond in the transition states are not significantly influenced by CO co-adsorption. Also, in the presence of CO, the reaction is less exothermic and the activation barrier is 0.12 eV higher than that of for single water splitting. This leads to considerable decrease in the reaction rate constant at 463 K, which is typical for low-temperature processes that include the WGS reaction [102], i.e., from \(2.03 \times 10^4\) s\(^{-1}\) to \(1.76 \times 10^3\) s\(^{-1}\) when CO is present. It may be noted that the difference in reaction rate constants in the absence and presence of CO increases with increasing temperature, and it becomes even more important to consider the effect of CO co-adsorption at higher temperatures.

The reason for the larger activation energy is probably the interplay between H\(_2\)O, CO and Ni surface, since the presence of the CO on the surface causes stronger interactions between the surface and the reactant and the products. The larger activation energy and decreased exothermicity in the presence of CO indicate that the stability induced by CO is larger for the reactant than for the transition state and product structures.
Figure 4.1 Reaction profiles for the water splitting reaction in the presence and absence of CO.

4.2 Paper II

Adsorption and dissociation of water on catalytic metal surfaces is of great importance in a variety of industrial processes. Therefore a detailed understanding of this process and how it is affected by the structure of the surface will assist in developing improved catalysts. In this paper, a comparative study of this process on the Ni(111), Ni(100) and Ni(110) surfaces, which is often used as catalyst, has been performed using DFT.

Different orientations of single adsorbates on all the adsorption sites shown in Figure 3.2 were geometry optimized and then the lowest energy structures were chosen for subsequent investigations of the reaction mechanism and rates. For co-adsorbed species, the initial structures for the optimizations were obtained by placing these species in the adjacent minimum energy sites (for the single adsorbates). The results are presented in Table 4.2.

According to the results, water is more stable on the Ni(110) surface and binds weakly through its oxygen atom on top of the Ni atom on all surfaces, and it is tilted near parallel with the surface. This is similar to previously obtained DFT results [85, 86] and experimental observations [103-106]. Similar to water, OH is more stable on the Ni(110) surface and binds to all surfaces via its oxygen atom. The preferred OH adsorption sites are F for Ni(110), D' for
Ni(100) and C' for Ni(111). For both H$_2$O and OH, the surface-adsorbate distance is smallest when the binding energy is strongest. The results obtained for OH are in agreement with previously calculated data when available [85, 86].

Table 4.2 Adsorption and co-adsorption energies (eV) for the chemical species involved in H$_2$O dissociation. Values are ZPVE-corrected.

<table>
<thead>
<tr>
<th>Species</th>
<th>surface</th>
<th>Adsorption site</th>
<th>$E_{ads}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>Ni(111)</td>
<td>A</td>
<td>−0.20</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>A</td>
<td>−0.27</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>A</td>
<td>−0.39</td>
</tr>
<tr>
<td>OH</td>
<td>Ni(111)</td>
<td>C'</td>
<td>−3.08</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>D'</td>
<td>−3.27</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>F</td>
<td>−3.44</td>
</tr>
<tr>
<td>O</td>
<td>Ni(111)</td>
<td>C'</td>
<td>−5.31</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>D'</td>
<td>−5.63</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>E</td>
<td>−4.98</td>
</tr>
<tr>
<td>H</td>
<td>Ni(110)</td>
<td>G</td>
<td>−2.51</td>
</tr>
<tr>
<td>OH + H</td>
<td>Ni(111)</td>
<td>OH: C', H: C'</td>
<td>−5.52</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>OH: D', H: D'</td>
<td>−5.80</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>OH: F, H: G</td>
<td>−6.09</td>
</tr>
<tr>
<td>O + H</td>
<td>Ni(111)</td>
<td>O: C', H: C'</td>
<td>−7.63</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>O: D', H: D'</td>
<td>−8.01</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>O: G, H: G</td>
<td>−7.84</td>
</tr>
</tbody>
</table>

Oxygen and hydrogen, unlike the water and OH, have the strongest bonding on the Ni(100) surface. The trends obtained here are in agreement with those previously calculated [85, 107-109]. For example, Fajín et al. [85] reported oxygen adsorption energies of −5.60 eV and −5.49 eV for the Ni(111) and Ni(110), respectively and Blaylock et al. [107] obtained adsorption energies of −4.81 eV and −5.46 eV for the Ni(111) and Ni(100) surfaces, respectively. The most stable adsorption sites for oxygen are C' on the Ni(111) surface, D' on Ni(100), and E on Ni(110), respectively. For hydrogen, the preferred sites are C' on the Ni(111) surface, D' on the Ni(100) surface and G on the Ni(110) surface, respectively. In contrast to water and OH, the surface-adsorbate distance for oxygen and hydrogen does not decrease with increasing adhesion strength.

All co-adsorbed species prefer the same adsorption sites as those found for the single adsorbates, except for the oxygen on the Ni(110) surface where the oxygen is shifted from the E to the G site.

Generally, adsorbates bind more strongly to the high symmetry sites than to the low symmetry sites, and to atoms with low coordination numbers rather than high coordination
numbers [9, 110, 111]. The surface metal atoms coordination numbers for the Ni(111), Ni(100) and Ni(110) surfaces are 9, 8 and 7, respectively. In addition, we have seen that all of the adsorbates are more negatively charged than when they are in vacuum [112]. This extra electron density is assumed to come from the frontier d orbitals of the metal surface. The intensities of the occupied orbitals at the Fermi level for the Ni(111), Ni(100) and Ni(110) surfaces are 2.0, 2.2 and 2.7 states/eV, respectively and therefore the Ni(110) surface can donate a higher electron density to the adsorbate. Hence, in agreement with this typical behaviour, water and OH have stronger adsorption energies on the Ni(110) and Ni(100) surfaces compared to the Ni(111) surface. In contrast, O and H have the strongest bonding on the Ni(100) surface. The reason is not clear, however, this is similar to what is reported in previous calculations which is further discussed in the paper.

The reaction profiles for the entire water dissociation process are compared in Figure 4.2. As it can be seen, the water splitting reaction is exothermic on all surfaces (see Figure 4.2(a)) and the activation barrier on Ni(110) is 0.07 eV and 0.31 eV lower than on the Ni(100) and Ni(111) surfaces, respectively. The water splitting rate constants are strongly influenced by the surface structure, and at 463 K they decrease from $7.36 \times 10^7$ s$^{-1}$ on Ni(110) to $7.62 \times 10^6$ s$^{-1}$ on Ni(100) and to $1.23 \times 10^4$ s$^{-1}$ on Ni(111). These results are supported by experimental observations [113-115] which are discussed in detail in the Section 3.2 in Paper II.

Similarly to water splitting, the lowest barrier for OH splitting is obtained on the Ni(110) surface. However, the barrier on the Ni(111) surface is lower than that for the Ni(100) surface. The OH splitting is endothermic on the Ni(110) surface, while it is exothermic on the other two surfaces. The rate constants at 463 K decrease from $1.43 \times 10^6$ s$^{-1}$ on Ni(110) to $1.14 \times 10^5$ s$^{-1}$ on Ni(111) and to $1.26 \times 10^3$ s$^{-1}$ on Ni(100).

Since, the difference in reaction rate constants significantly increases with increasing temperature [58, 112], it becomes even more important to consider the effect of surface configuration at elevated temperatures.

The d-band centre describes the distribution of surface electronic energy levels [116, 117] and the ability to eject an electron from the d-band of the metal to the adsorbate. This can explain differences in catalytic activity of the different surfaces. The calculated d-band centres are at $-1.75$, $-1.98$ and $-2.08$ eV for the Ni(110), Ni(100) and Ni(111) surfaces, respectively. Generally, the surface is more reactive when the d-band centre is closer to the Fermi level [116, 117]. As expected, the reaction barrier for the water and OH splitting on the three surfaces is the lowest on the Ni(110) surface, which has a d-band centre that is closest to the Fermi level.

Based on the rate constants obtained from DFT, a kinetics model was developed to investigate the overall water dissociation reaction (for more details see Section 2.3 in Paper II). The results showed that the overall reaction is fastest on Ni(110) and follows the order Ni(110) > Ni(100) > Ni(111).
4.3 Paper III

Formyl plays a key role in industrial processes such as water gas shift (WGS), Fischer Tropsch synthesis (FTS) and catalytic hydrocarbon combustion reactions. In this paper, the adsorption, reaction and activation energies of formyl oxidation and dissociation on the Ni(111), Ni(100) and Ni(110) surfaces were investigated using DFT calculations. Same procedure as explained in Section 4.2 was used here to calculate the adsorption energies. For calculating the co-adsorption energies, all possible adsorption sites were examined for the
isolated molecules involved in the reactions. The initial structures for the geometry optimizations of co-adsorbed species were obtained by placing the adsorbates in their minimum energy sites (for the isolated adsorbates). The geometry optimized structures that had the lowest energies were then selected for further investigations of the reaction mechanisms. The results obtained are presented in Table 4.3.

**Table 4.3** Adsorption and co-adsorption energies (eV) for the chemical species involved in formyl oxidation and dissociation. Values are ZPVE-corrected.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>Site</th>
<th>$E_{ads}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCOO</td>
<td>Ni(111) O: A O2: A</td>
<td>-2.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(100) O: B O2: A</td>
<td>-2.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(110) O: A O2: A</td>
<td>-3.29</td>
<td></td>
</tr>
<tr>
<td>CHO</td>
<td>Ni(111) C: B O: A</td>
<td>-2.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(100) C: B O: B</td>
<td>-2.76</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(110) C: F O: A</td>
<td>-2.42</td>
<td></td>
</tr>
<tr>
<td>CHO + O</td>
<td>Ni(111) C: B, OCHO: A, O: C'</td>
<td>-6.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(100) C: B, OCHO: B, O: D'</td>
<td>-7.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(110) C: F, OCHO: A, O: G</td>
<td>-7.63</td>
<td></td>
</tr>
<tr>
<td>CH + O</td>
<td>Ni(111) C: C' O: C'</td>
<td>-10.81</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(100) C: D' O: D'</td>
<td>-12.28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(110) C: D O: G</td>
<td>-11.89</td>
<td></td>
</tr>
<tr>
<td>CO + H</td>
<td>Ni(111) C: C H: C'</td>
<td>-4.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(100) C: D' H: D'</td>
<td>-4.61</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(110) C: F H: G</td>
<td>-4.51</td>
<td></td>
</tr>
</tbody>
</table>

It can be seen that the formate (HCOO) adsorption strength decreases in the order Ni(110) > Ni(100) > Ni(111). As discussed in Section 4.2, the trends of adsorption energies obtained are expected. The HCOO adsorb bidentately to all three surfaces via its two oxygen atoms. Both oxygen atoms of the formate are over the top site on the Ni(111) and Ni(110) surfaces. However, on the Ni(100) surface one oxygen is over a top site, A, and the other one is over a bridge site, B.
For CHO the strongest adsorption was obtained for the Ni(100) surface which is in contrast to the trend that molecules bind most strongly to the Ni(110) surface. The reason could be the orientation of the formyl molecule on the Ni(100) surface. The C-O bond is almost parallel to this surface, while the carbon atom points towards the surface on the other two surfaces.

Except for oxygen on the Ni(110) surface, in all cases the co-adsorption sites are the same as those found for the isolated adsorbates. The strongest adsorption energy for O on the Ni(110) surface was obtained at the long bridge site E, whereas the co-adsorbed CHO shifts the oxygen from the E to the G site.

The co-adsorption is strongest on the Ni(100) surface similarly to CHO. Also, similarly to CHO, co-adsorption of CHO + O and CH + O is stronger on the Ni(110) surface than on the Ni(111) surface. Although CO + H co-adsorption is stronger on the Ni(111) surface than on the Ni(110) surface.

The reaction profiles for the oxidation and dissociation of formyl are shown in Figure 4.3 together with the structures of the reactants, transition states and products. For oxidation of formyl, the activation energy is lowest on the Ni(111) surface and the reaction is exothermic on all surfaces (see Figure 4.3(a)).

The obtained activation energies for dissociation of formyl to CH and O (see Figure 4.3(b)) are 1.16 eV, 1.86 eV and 0.89 eV for the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The reaction is endothermic on the Ni(111) surface whereas it is exothermic on the other two surfaces.

The dissociation of formyl to CO and H over all three surfaces is exothermic and the obtained activation energies are 0.15 eV, 0.48 eV and 0.16 eV for the Ni(111), Ni(100) and Ni(110) surfaces, respectively (see Figure 4.3(c)).

The calculated energetics is in agreement with previous experimental and theoretical results. This is further discussed in Paper III.

It can be seen from Figure 4.3 that the activation barriers for CHO dissociation to CO and H are smaller on all surfaces compared to the oxidation reaction and the dissociation of CHO to CH and O. Therefore, the adsorbed formyl species are far more likely to dissociate to CO and H than to react with a co-adsorbed oxygen atom or to dissociate to CH and O.

No consistent correlations were found between the transition state geometries and the surface atom charge densities or surface d-band centres (which are previously discussed in Section 4.2 as the origins of the catalytic activity of these nickel surfaces). Although the energetics obtained for formyl oxidation and for dissociation to CO + H support the BEP principle with R^2 values of 0.94 and 0.78. The R^2 value for CHO dissociation to CH and O is 0.10.
Figure 4.3 Reaction profiles for the (a) water and (b) OH splitting over Ni(111) (solid black line), Ni(100) (long-dashed blue line) and Ni(110) (short-dashed red line).
4.4 Paper IV

Combustion and synthesis of hydrocarbons may occur directly (CH → C + H and CO → C + O) or via a formyl (CHO) intermediate. In Paper IV, the energetics of these reactions is investigated on Ni(111), Ni(100) and Ni(110) surfaces.

4.4.1 Catalytic hydrocarbon combustion

The activation and reaction energies for the catalytic combustion of hydrocarbons are given in Table 4.4.

<table>
<thead>
<tr>
<th>Surface</th>
<th>CH → C + H</th>
<th>CH + O → CHO</th>
<th>CHO → CO + H</th>
</tr>
</thead>
<tbody>
<tr>
<td>E&lt;sub&gt;a&lt;/sub&gt;</td>
<td>ΔE</td>
<td>E&lt;sub&gt;a&lt;/sub&gt;</td>
<td>ΔE</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>1.15</td>
<td>0.49</td>
<td>0.85</td>
</tr>
<tr>
<td>Ni(100)</td>
<td>0.45</td>
<td>−0.21</td>
<td>2.46</td>
</tr>
<tr>
<td>Ni(110)</td>
<td>0.33</td>
<td>−0.22</td>
<td>1.43</td>
</tr>
</tbody>
</table>

For dissociation of CH, the calculated activation energies are 1.15 eV, 0.45 eV and 0.33 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The reaction is endothermic on the Ni(111) surface while as it is exothermic on the other two surfaces.

The lowest activation barrier for methylidyne oxidation was obtained on the Ni(111) surface, i.e., 0.85 eV compared to 2.46 eV and 1.43 eV on the Ni(100) and Ni(110) surfaces, respectively. The oxidation reaction is endothermic on the Ni(100) and Ni(110) surfaces whereas it is exothermic on the Ni(111) surface.

The activation energies for CHO dissociation to CO and H are 0.15 eV, 0.0.48 eV and 0.16 eV for the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The trend is the same as CH oxidation, and the reaction is exothermic on all surfaces.

The geometries of the reactants, transition states and products which are presented in Table 4.4, are shown in Figure 4.4(a). The adsorption and co-adsorption energies together with the details of these structures are given in Tables S1, S3 and S4 in the Supporting Information of Paper IV.
The calculations reveal that the fraction of CH that undergoes direct dissociation prior to oxidation is very small due to its higher activation barrier (1.15 eV compared to 0.85 eV) when there is sufficient co-adsorbed oxygen on the Ni(111) surface.
On the Ni(100) and Ni(110) surfaces, in contrast, the CH dissociation barrier is lower than the
its oxidation barriers. This means that the direct dissociation of CH to C and H is preferred to
oxidation via a CHO intermediate on these surfaces, since the barrier for formation of CHO
intermediate is about five times larger than that of for the direct dissociation. The reaction rate
constants (k values given in Table 1 in Paper IV) for CH and CHO dissociation are largest
on the Ni(110) surface as expected regarding the d-band centre discussed before. Although,
the rate constant for CH oxidation is bigger on the Ni(111) surface compared the other
surfaces.

4.4.2 Catalytic hydrocarbon synthesis

The activation barriers and reaction energies calculated for the catalytic hydrocarbon
synthesis are given in Table 4.5.

<table>
<thead>
<tr>
<th>Surface</th>
<th>CO → C + O</th>
<th>CO + H → CHO</th>
<th>CHO → CH + O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$</td>
<td>$\Delta E$</td>
<td>$E_a$</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>2.99</td>
<td>2.60</td>
<td>1.53</td>
</tr>
<tr>
<td>Ni(100)</td>
<td>1.98</td>
<td>0.82</td>
<td>1.36</td>
</tr>
<tr>
<td>Ni(110)</td>
<td>1.83</td>
<td>0.76</td>
<td>1.29</td>
</tr>
</tbody>
</table>

The lowest activation energy for CO dissociation is on the Ni(110) surface, and is 1.83 eV
compared to 2.99 eV and 1.98 eV on the Ni(111) and Ni(100) surfaces, respectively, and the
reaction is endothermic on all three surfaces.

For the hydrogenation of CO, the activation barrier obtained are 1.53 eV, 1.36 eV and 1.29
eV for the Ni(111), Ni(100) and Ni(110) surfaces, respectively. Similarly to the dissociation
reaction, the lowest barrier is obtained on the Ni(110) surface, and the reaction is endothermic
on all surfaces.

For formyl dissociation to CH and O, however, the obtained barrier decreases in the order
Ni(100) > Ni(111) > Ni(110). The reaction is endothermic on the Ni(111) surface while it is
exothermic on the Ni(110) and Ni(100) surfaces.

Figure 4.4(b) shows geometries of the reactants, transition states and products for the
reactions given in Table 4.5. The adsorption and co-adsorption energies together with the
details of these structures are given in Tables S2, S3 and S4 in the Supporting Information of
Paper IV.
The activation energies on the different surfaces increases in the order Ni(110) < Ni(100) < Ni(111) except for CHO dissociation to CH and O, where the barrier on the Ni(100) surface is higher compared to the Ni(111) surface.

The activation energies for dissociation of CO are higher on all surfaces compared to its hydrogenation. The obtained CO adsorption energies are –1.89 eV, –1.96 eV and –1.89 eV on the Ni(111), Ni(100) and Ni(110), respectively. Thus, dissociation of CO is favoured on the Ni(110) surface while on the Ni(111) and Ni(100) surfaces, CO desorption will compete with dissociation. However, the activation energies for hydrogenation of CO are lower than those for its dissociation and desorption on all surfaces. Therefore, the adsorbed CO species is more likely to react with co-adsorbed hydrogen than to dissociate to C and O or to desorb from the surface, when hydrogen is co-adsorbed on the Ni surface.

Based on the results of DFT calculations, a kinetic model was used to investigate the time dependence of the CH concentration produced via the direct dissociation route (CO ⇌ C + O followed by C + H → CH) and the formyl route (CO + H ⇌ CHO followed by CHO → CH + O) on the three different Ni surfaces. The reaction rate constants calculated at 600 K, which is
a typical temperature for synthesis and low temperature catalytic combustion of hydrocarbons [118-120], and the initial concentration of adsorbed CO and H are 1 (arbitrary units of concentration). Figure 4.5 shows the average CH formation rate from each CO molecule on the surface, therefore the concentration of the produced CH increases until it reaches 1. As it can be seen, both routes are fastest on the Ni(110) surface. Also, on the Ni(110) and Ni(100) surfaces, the direct route is faster, while the formyl route will dominate on the Ni(111) surface. Different H concentrations (between 0.25 and 1.5) were used in the kinetics model and yielded the same trends. It may be noted that the calculated the rate constants (see Table 2 in Paper IV) for synthesis reactions are far smaller than those for the combustion reactions (see Table 1 in Paper IV). Thus Ni is a better catalyst for hydrocarbon combustion.

4.5 Paper V

In Paper V, the water gas shift reaction (WGS) reaction was studied by looking at the adsorption energies for ten species involved in the reaction together with activation barriers and reaction energies for the nine most important elementary steps using DFT calculations.

The structures of the adsorbed and co-adsorbed species involved in the WGS reaction were obtained using the same procedure explained in Paper III and Paper IV. The trends obtained for adsorption and co-adsorption energies are further discussed in the Paper V and the details of the structures are given in Supporting Information of the paper. These structures were then selected for investigations of the reaction mechanism.

The activation and reaction energies of all the elementary steps (R1-R9) are summarized in Table 4.6. Details of the structures of the reactants, products and transition states are given in the Supporting Information of the paper (Tables S1-S9 and Figures S1-S9).

The adsorbed carbon monoxide cannot react directly with H$_2$O [14, 121]. So, the WGS reaction starts by H$_2$O splitting to OH and H. The activation energies of both H$_2$O and OH splitting reactions follow the order Ni(100) > Ni(111) > Ni(110). The barriers of the H$_2$O splitting are larger than the adsorption energies of the water on both the Ni(111) and Ni(100) surfaces. Hence, it is expected that most of the H$_2$O molecules desorb without proceeding to OH + H species. On the Ni(110) surface, in contrast, the calculated adsorption energy is slightly higher than the splitting barrier. Experimental studies, which are further discussed in the paper, support these results [113-115].
Table 4.6 The activation and reaction energies (eV) for the elementary steps of the WGS reaction. The activation and reaction energies are for the forward reactions and the values are ZPVE-corrected.a

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Surface</th>
<th>$E_a$(eV)</th>
<th>$\Delta E$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1: $\text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{H}$</td>
<td>Ni(111)</td>
<td>0.67</td>
<td>$-0.20$</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>0.76</td>
<td>$-0.63$</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>0.38</td>
<td>$-0.56$</td>
</tr>
<tr>
<td>R2: $\text{OH} \rightleftharpoons \text{O} + \text{H}$</td>
<td>Ni(111)</td>
<td>0.79</td>
<td>$-0.03$</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>1.05</td>
<td>$-0.45$</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>0.61</td>
<td>0.14</td>
</tr>
<tr>
<td>R3: $\text{CO} + \text{O} \rightleftharpoons \text{CO}_2$</td>
<td>Ni(111)</td>
<td>1.35</td>
<td>0.65$^b$</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>1.25</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>1.57</td>
<td>0.72</td>
</tr>
<tr>
<td>R4: $\text{CO} + \text{OH} \rightleftharpoons \text{COOH}$</td>
<td>Ni(111)</td>
<td>1.30</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>1.73</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>1.44</td>
<td>1.18</td>
</tr>
<tr>
<td>R5: $\text{COOH} \rightleftharpoons \text{CO}_2 + \text{H}$</td>
<td>Ni(111)</td>
<td>0.68</td>
<td>$-0.02$</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>1.21</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>1.07</td>
<td>0.08</td>
</tr>
<tr>
<td>R6: $\text{CO} + \text{H} \rightleftharpoons \text{CHO}$</td>
<td>Ni(111)</td>
<td>1.53</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>1.36</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>1.29</td>
<td>1.13</td>
</tr>
<tr>
<td>R7: $\text{CHO} + \text{O} \rightleftharpoons \text{HCOO}$</td>
<td>Ni(111)</td>
<td>0.67</td>
<td>$-0.85$</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>1.47</td>
<td>$-0.10$</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>0.99</td>
<td>$-0.72$</td>
</tr>
<tr>
<td>R8: $\text{HCOO} \rightleftharpoons \text{CO}_2 + \text{H}$</td>
<td>Ni(111)</td>
<td>2.74</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>2.76</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>1.07</td>
<td>0.43</td>
</tr>
<tr>
<td>R9: $\text{H} + \text{H} \rightleftharpoons \text{H}_2$</td>
<td>Ni(111)</td>
<td>0.81</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>0.88</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>0.42</td>
<td>0.36</td>
</tr>
</tbody>
</table>

a The data for CHO, HCOO and CO are taken from our previous studies [122, 123]. b This is the value before ZPVE corrections.

CO can react with the products of the H$_2$O splitting (OH, O and H) via three different pathways including the direct, carboxyl and formate.

In the direct (or redox) pathway, CO$_2$ is produced by the reaction between carbon monoxide and oxygen. The reaction is endothermic on all surfaces and the lowest activation barrier obtained on the Ni(100) surface which is 1.25 eV compared to 1.35 eV and 1.57 eV on the Ni(111) and Ni(110) surfaces, respectively.

In the carboxyl pathway, adsorbed CO endothermically reacts with the OH and COOH is produced. The calculated activation energies are 1.30 eV, 1.73 eV and 1.44 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. Then, COOH dissociates to CO$_2$ and H with activation energies of 0.68 eV, 1.21 eV and 1.07 eV on the Ni(111), Ni(100) and Ni(110)
surfaces, respectively. This step is slightly exothermic on the Ni(111) surface, whereas it is endothermic on the other two surfaces.

In the formate pathway, the adsorbed CO reacts with an adsorbed H atom to produce CHO. The reaction is endothermic on all three surfaces and activation barriers are 1.53 eV, 1.36 eV and 1.29 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The experimental values reported for CO hydrogenation on the Ni(111) and Ni(100) surfaces are 1.67 eV [124] and 1.07 eV [125], respectively, which support the trends presented here. The formyl is then exothermically oxidized to formate with activation barriers of 0.67 eV, 1.47 eV and 0.99 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The HCOO subsequently dissociates to CO$_2$ and H. The calculated activation energies for this step are 2.74 eV, 2.76 eV and 1.07 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively, and the reaction is endothermic on all three surfaces. HCOO has a high barrier for dissociation which could explain why the formate is the most frequently observed intermediate in WGS experiments [26, 27, 126-129].

Finally, the adsorbed H atoms produce H$_2$ which subsequently desorbs. The obtained activation barriers are 0.81 eV, 0.88 eV and 0.42 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively, and the reaction is endothermic on all three surfaces. It may be noted that the calculated activation energies are slightly smaller than the reaction energies on Ni(111) and Ni(100) surfaces. However, this is within the statistical uncertainty of the method since DFT-GGA accuracy is about 0.1 eV [130]. The similarity of $E_a$ and $\Delta E$ has also been seen previously by Lin et al. [14] and Catapan et al. [6]. They found a difference of 0.03 eV and 0.08 eV between $E_a$ and $\Delta E$ on the Ni(111) surface, respectively.

The trends found for reactions R1, R2, R6, R8 and R9 can be explained by d-band centre of three nickel surfaces (which is discussed in detail in Paper II). However, for reactions R4, R5 and R7 the lowest barrier is obtained on the Ni(111) surface, and for R3 the lowest barrier is obtained on the Ni(100) surface.

The energy profiles for the direct, carboxyl and formate pathways of CO oxidation to carbon dioxide on the Ni(111), Ni(100) and Ni(110) surfaces are shown in Figure 4.6. For the Ni(111) surface, the direct and the carboxyl pathways are preferred to as a result of the lower barriers for consuming carbon monoxide. The activation barrier of forming CO$_2$ via the direct pathway (R3) is 1.35 eV. COOH is produced via the carboxyl pathway (R4), where the activation energy is 1.30 eV, and then dissociate to CO$_2$ and H (R5) with a barrier of 0.68 eV. Although, the barrier for the reverse reaction of R4 is almost half of the R5 reaction barrier, i.e., 0.31 eV compared to 0.68 eV. Therefore, the rate of formation of CO$_2$ via carboxyl pathway is lowered by the two activation barriers (R4 and R5) and the reverse of R4 (COOH → CO and OH) is faster than R5.

The CO hydrogenation (R6) barrier is about 0.2 eV higher compared to its oxidation (R3 in the direct pathway), and the dissociation barrier of the produced CHO (via the reverse of reaction R6) is considerably lower than the activation barrier of R7 (formate production). In addition, the barrier of formate dissociation to CO$_2$ and H is very large (2.74 eV) which makes reaction via the formate pathway very slow.
Therefore, on the Ni(111) surface, the direct pathway is favoured and the reaction R3 (CO + O → CO₂) is the rate limiting step.

Figure 4.6 Reaction profiles for the WGS reaction on (a) Ni(111), (b) Ni(100) and (c) Ni(110) via direct (long-dashed blue line), carboxyl (short dashed green line) and formate pathways (solid orange line).
For the Ni(100) surfaces, a similar analysis shows that the direct pathway is preferred since the reaction barrier for carbon dioxide consumption in this pathway (R3: 1.25 eV) is smaller than in the carboxyl pathway (R4: 1.73 eV) and in the formate pathway (R6: 1.36 eV). The produced formyl via R6 can be oxidized to formate (R7) which is a stable intermediate due to its large barrier for carbon dioxide production (R8: 2.76 eV) and the high barrier for its dissociation to CHO and O (reverse of R7, 1.47 eV). The formyl can also dissociate to CO and H (reverse of R6) instead of oxidizing to CO₂ (R7), as the barrier of its dissociation (reverse of R6) is almost one third of the barrier for its oxidation (R7), i.e., 0.48 compared to 1.47 eV.

Hence, on the Ni(100) surface, the direct pathway is the main route of the WGS reaction and the rate determining step is the oxidation of carbon dioxide (R3).

For the Ni(110) surface, the hydrogenation of CO (R6) has a lower barrier (1.29 eV) than CO oxidation (R3, direct pathway, 1.57 eV) or CO reacting with OH (R4, carboxyl pathway, 1.44 eV). The produced CHO via reaction R6, however, has a large barrier (0.99 eV) to form formate via R7, and the barrier of the reverse of R6 is very low compared to R7, i.e., 0.16 eV compared to 0.99 eV. This further hinders the formation of formate via R7, and indicates that the formate pathway is not the route for CO₂ production.

The reaction involving CO with OH (R4) to form COOH has a barrier of 1.44 eV, and the barrier for COOH dissociation to carbon dioxide and hydrogen (R5) is 1.07 eV. However, the barrier for the reverse of R4 is far smaller than the barrier of R5, i.e., 0.26 eV compared to 1.07 eV, which reduces the rate of CO₂ production via the carboxyl pathway.

Consequently, CO₂ is primarily produced via the direct pathway, similarly to the other two surfaces, and R3 is the rate limiting step.

According to the trends obtained for activation barrier of reaction R3, the direct pathway on the Ni(100) will be the dominant mechanism on all three Ni surfaces if O intermediates are present on the surface. However, the barriers for water dissociation are larger than desorption energies on the Ni(111) and Ni(100) surfaces. Therefore, at low H₂O(g) pressures the direct pathway on the Ni(110) will dominate.

In addition to the energetics, the main pathway of CO₂ formation depends on the coverage of the co-reactant, O, which favours the direct path, OH, which favours the carboxyl path, or H, which favours the formate path.

The results obtained from the DFT calculations are consistent with previous theoretical and experimental investigations [6, 14, 19, 131-141] which are further discussed in the Paper V. For example, Hilaire et al. [135] studied the WGS reaction over ceria supported metallic catalysts including nickel. Their study showed that the mechanism for the reaction involves a direct pathway.

The results obtained here support the validity of the TSS method. The data yield an equation of \( E_{TS} = 0.96 \ E_{FS} - 3.20 \) with a \( R^2 \) value of 0.99. It should be noted that only three Ni facets
have been studied in this work, and studies of more facets would improve the statistical relevance of the results.

4.6 The transition state scaling for Papers II-V

Figure 4.7 shows the TSS correlations for all the reactions studied in Papers II-V (Paper I is excluded, since a different supercell size is used for the calculations). As it can be seen, the results support the TSS method and yield an equation of $E_{TS} = 0.96 \times E_{FS} - 2.91$ with a $R^2$ value of 0.99. The activation barrier for other reactions occurring on these nickel facets can therefore be estimated by this reaction. Those activation barriers can then be used for kinetic modelling which is a part of the future work.

![Figure 4.7 The transition state scaling (TSS) relation for all of the studied reactions on the Ni(111), Ni(100), and Ni(110) surfaces.](image-url)
Density functional theory (DFT) calculations were used to study the effect of co-adsorption of water and CO on the Ni(111) surface as well as the water adsorption and dissociation, formyl oxidation and dissociation, hydrocarbon combustion and synthesis, and the WGS reaction on Ni(111), Ni(100) and Ni(110) surfaces.

The results show that:

- The co-adsorption of CO alters the geometry of the adsorbed reactant water molecule. The O-H bond that is closest to the carbon monoxide is lengthened and weakened. The distance between the surface and the reactants and products decreases in the presence of the co-adsorbed CO. These changes lead to a dissociation energy that is 0.24 eV less exothermic, and to an activation energy for H\(_2\)O dissociation which is 0.12 eV higher in the presence of the co-adsorbed CO. At 463 K, the rate constant in the presence of CO is about twelve times smaller than in the absence of CO. Therefore, it is important to account for co-adsorbed carbon monoxide when water dissociation occurs on nickel surface in a CO-rich environment.

- For adsorption and dissociation of water, the H\(_2\)O and OH adsorbates bind more strongly to the less packed Ni(110) and Ni(100) surfaces compared to the highly packed Ni(111) which is in agreement with the fact that the d-band center of the Ni(110) surface is closer to the Fermi level than for the other two surfaces. However, O and H bind strongest to the Ni(100) surface. At 463 K, the overall reaction rate for the entire water dissociation reaction decreases in the order Ni(110) > Ni(100) > Ni(111).

- For the formyl dissociation, the barrier for \(\text{CHO} \rightarrow \text{CH} + \text{O}\) (FTS process) is higher than that for \(\text{CHO} \rightarrow \text{CO} + \text{H}\) (catalytic combustion) on all three surfaces, and
reaction rate constant decreases in the order Ni(110) > Ni(111) > Ni(100). For oxidation of formyl (CHO + O → HCOO), the lowest activation energy is on the Ni(111) surface and increases in the order Ni(111) < Ni(110) < Ni(100). The barrier for CHO → CH + O and CHO + O → HCOO is seven and four times higher, respectively, compared to CHO → CO + H on the Ni(111) surface. Therefore, at 463K, the rate constant for CHO → CO + H is $3 \times 10^{12}$ and $3 \times 10^6$ times larger than those for formate formation and formyl dissociation to CH and O. The barrier for dissociation of CHO to CO and H is lower compared to the other two reactions irrespective of the crystallographic structure of the Ni surfaces. Hence, formyl prefers to dissociate to CO and H instead of reacting with co-adsorbed oxygen atoms or dissociating to CH and O. Consequently, nickel performs better for this reaction (catalytic combustion) compared the FTS process. The results also show that the WGS reaction with a Ni catalyst does not, to a large extent, occur via the formate pathway.

For catalytic hydrocarbon combustion, the CH dissociation is favoured on the Ni(110) and Ni(100) surfaces, while its oxidation to CHO is favoured on the Ni(111) surface. The dissociation barrier increases in the order Ni(110) < Ni(100) < Ni(111) and the oxidation barrier decreases in the order Ni(100) > Ni(110) > Ni(111). The barrier for formyl dissociation to CO and H follows the same order as CH oxidation. For the catalytic hydrocarbon synthesis, the CO hydrogenation to CHO is favoured over nickel in the presence of sufficient co-adsorbed H, since the CO dissociation barrier is significantly higher compared to its hydrogenation barrier on all three nickel surfaces. The rate of both reactions decreases in the order Ni(110) > Ni(100) > Ni(111). Based on DFT calculations, the Ni(110) surface showed a better catalytic activity for hydrocarbon combustion than for hydrocarbon synthesis. The d-band centre can explain the relative catalytic activity of all facets of the Ni surface, except for CH oxidation which is faster on the Ni(111) surface. All reactions studied support the BEP relations with $R^2$ values of 0.85 for C-H bond breaking/forming and 0.72 for C-O bond breaking/forming.

For the WGS reaction, H$_2$O, OH, HCOO, CO$_2$ and H$_2$ bind strongest to the Ni(110) surface whereas COOH, CHO, CO, O and H bind strongest to the Ni(100) surface. The lowest barrier obtained for the water dissociation (reactions R1 and R2), formyl formation (R6), formate dissociation (R8) and H$_2$ formation (R9) obtained on the Ni(110) surface, while the lowest barrier for CO oxidation to CO$_2$ (R3) is on the Ni(100) surface. Analysis of energetics indicates that the direct (redox) pathway is favoured on all three surfaces via the reaction CO + O → CO$_2$ as the rate determining step. The barrier obtained for this elementary step decreases in the order Ni(110) > Ni(111) > Ni(100). Hence the Ni(100) surface is more active for the WGS reaction compared to the other surfaces if adsorbed oxygen atoms are present. Although, due to higher barriers for H$_2$O dissociation than for H$_2$O desorption on the Ni(111) and Ni(100) surfaces, the direct pathway on the Ni(110) will dominate at low H$_2$O(g) pressures. The results also reveal that formate is a stable intermediate on all surfaces due to its high dissociation barriers which can explain the experimental observations.
of formate on Ni surfaces. Hence, formate is not an active species in the conversion of CO to carbon dioxide in the WGS reaction. BEP relationships are valid for the studied reactions on these surfaces, with an $R^2$ value of 0.99.
Understanding the mechanisms of heterogeneous catalytic processes is of great importance in order to improve the efficiencies and to identify optimal catalysts and operating conditions. The following investigations are suggested for the future work:

- Kinetic modelling of the WGS reaction using DFT results
- The steam methane reforming (SMR) over Ni different facets where nickel is frequently used as the catalyst
- Hydrocarbon combustion and synthesis on different transition metals to investigate the catalytic activity of the transition metals during these processes
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Abas Mohsenzadeh

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The Effect of Carbon Monoxide Co-Adsorption on Ni-Catalysed Water Dissociation

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Abstract: The effect of carbon monoxide (CO) co-adsorption on the dissociation of water on the Ni(111) surface has been studied using density functional theory. The structures of the adsorbed water molecule and of the transition state are changed by the presence of the CO molecule. The water O–H bond that is closest to the CO is lengthened compared to the structure in the absence of the CO, and the breaking O–H bond in the transition state structure has a larger imaginary frequency in the presence of CO. In addition, the distances between the Ni surface and H₂O reactant and OH and H products decrease in the presence of the CO. The changes in structures and vibrational frequencies lead to a reaction energy that is 0.17 eV less exothermic in the presence of the CO, and an activation barrier that is 0.12 eV larger in the presence of the CO. At 463 K the water dissociation rate constant is an order of magnitude smaller in the presence of the CO. This reveals that far fewer water molecules will dissociate in the presence of CO under reaction conditions that are typical for the water-gas-shift reaction.

Keywords: water adsorption; water dissociation; nickel; water gas shift reaction; CO; H₂O; DFT
1. Introduction

The water gas shift (WGS) reaction, \( \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \), is important in many industrial processes, including methanol synthesis and production of hydrogen for use in, e.g., fuel cells. It is also one of the most important reactions in gasification, where carbonaceous materials are converted to a gaseous product that can be used to produce energy or other desirable chemicals [1–5]. The efficiency of the WGS reaction is enhanced in the presence of transition metal catalysts such as nickel, which is widely used due to its high heat conductivity, high catalytic conversion and its capability to be manufactured in different shapes [6–9].

Due to its industrial significance, several experimental and computational investigations have focused on the WGS reaction. Bond et al. proposed a modified route for the gold-catalyzed WGS reaction mechanism by thermal decomposition of a carboxyl species [10]. Steady-state WGS kinetics were determined on ceria-supported Pd, Pt and Rh catalysts by Gorte et al.; they found that the ceria structure significantly affects the results [11]. Shekhar et al. have investigated the promotional effect of alkali additives (Na, Li and K) on the WGS reaction for Pt/Al\(_2\)O\(_3\) and Pt/TiO\(_2\) catalysts. They showed that the active platinum remains in the metallic state and that the promotion by alkali is due the modification of the support properties [12]. A density functional theory (DFT) study together with experimental data for the WGS reaction catalyzed by Pt were provided by Gokhale et al. They predicted that that the most significant reaction channel proceeds via a carboxyl intermediate while formate acts only as a spectator species [13]. Furthermore, Cordeiro et al. studied the role of the step sites in the WGS reaction catalyzed by Cu and found that the associative route through the carboxyl intermediate assisted by co-adsorbed OH is favored in the presence of steps [14].

The four mechanisms that have been suggested for the WGS reaction are the redox, formate, associative and carbonate mechanisms [15–27]. Previous first principles calculations showed that the most probable reaction mechanisms are the carboxyl and redox mechanisms, and that the rate-limiting step is water dissociation [14,15,28–33].

The catalytic dissociation of water is also important in many other industrial processes, such as steam methane reforming (SMR; \( \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \)) where nickel is frequently used as catalyst. The SMR reaction involves the conversion of a hydrocarbon fuel (or an alcohol) into another fuel containing higher heating value. The SMR reaction is widely implemented for production of hydrogen or other useful products [34–36]. The water dissociation is believed to be one of the rate controlling elementary reaction steps in the SMR reaction [37].

The catalytic dissociation of water has been widely studied using both experimental and computational techniques. For example, hydroxyl radical production following Ni-catalyzed water dissociation has been investigated experimentally by Keiser et al. [38]. The hydroxyl radicals were monitored using laser-induced fluorescence and the barrier for their desorption was estimated at different temperatures and pressures. Fajín et al. studied water dissociation on metal surfaces using DFT. They predicted that the nickel surface could be effective for catalyzing water dissociation, that the activation barrier is 0.71 eV and the reaction energy is \(-0.37\) eV [33]. The binding energies, preferred adsorption sites and configurations for water and its dissociation products (OH and H) were determined over a number of surfaces, including Ni(111), by Phatak et al. They found that dissociation of H\(_2\)O to OH and H is exothermic on Ni(111) and the activation and reaction energies are 0.96 eV and \(-0.2\) eV,
respectively [39]. Several studies have also focused on fundamental aspects of water dissociation on metal surfaces, such as the vibrational modes of the molecular and dissociated water [40–44].

In addition to the WGS reaction discussed above, interaction of CO with transition metal surfaces is of importance in many catalytic reactions, such as the oxidation of carbon monoxide, CO methanation and Fischer-Tropsch synthesis [45]. These interactions, including the interactions between adsorbed CO and H\textsubscript{2}O, have been investigated over Ni(111) [46–48]. For example, high resolution electron energy loss spectroscopy (HREELS) measurements by Ellis \textit{et al.} revealed strong interaction between H\textsubscript{2}O and CO adsorbed on Ni(100), where the co-adsorbed CO changes the water OH stretching properties [49]. DFT calculations by Lin \textit{et al.} yielded a reaction energy of $-0.11$ eV and an activation barrier of 0.79 eV for water dissociation in the presence of CO [50]. This reaction energy is less exothermic than those obtained in the absence of CO ($-0.37$ and $-0.2$ eV, see above) and the activation barrier lies between the values obtained in the absence of CO (0.71 and 0.96 eV). These, and other co-adsorption studies of reactive chemical species on transition-metal catalysts, [51–54] are essential for a more complete understanding of heterogeneous catalysis.

The present contribution extends these previous investigations by using DFT to perform a comparative study of the dissociation of water on a Ni(111) surface in the absence and presence of co-adsorbed CO. This is the first time that these systems have been studied using the same models and computational methods, and is important since, if the co-adsorbed CO affects the reactant, transition state or product relative energies or vibrational frequencies, then the water dissociation rate will depend on the presence of CO. For example, the rates may be different for the reaction in a CO-rich WGS and when water dissociates in other processes when CO is not present. In addition, molecular-level understanding of the water dissociation mechanism which, as discussed above, is a key elementary step in a number of important reactions such as WGS and SMR, will assist in designing more effective catalysts.

2. Results and Discussion

2.1. Adsorption Sites and Energies

The top (t), hollow hcp (h) and hollow fcc (f) sites on the Ni(111) surface are shown in Figure 1. Geometry optimization of the reactants and products was performed on the sites that have previously been shown [50] to yield the lowest energy structures (\textit{i.e.}, the most favorable sites). The lowest energy structures in the absence and presence of CO are shown in Figures 2 and 3, respectively, and details of these structures are shown in Table 1. The * in these figures and table indicates that the specie is adsorbed on the surface.

In the absence of CO, the preferred adsorption site for water is the top site (t) via the O atom. The adsorption energy is $-0.27$ eV ($-0.36$ eV without zero point vibrational energy [ZPVE] correction). Both of the OH and H products favor the hollow fcc site (f) and, similarly to the water molecule, the OH is adsorbed via the O atom. The adsorption energy of these products is $-5.83$ eV ($-6.23$ eV without ZPVE correction).
**Figure 1.** Top (t), hollow hcp (h) and hollow fcc (f) sites on the Ni(111).

**Figure 2.** Minimum energy structures of the reactant, transition state and product for the $\text{H}_2\text{O}^* \rightarrow \text{OH}^* + \text{H}^*$ reaction.

**Figure 3.** Minimum energy structures of the reactant, transition state and product for the $\text{H}_2\text{O}^* + \text{CO}^* \rightarrow \text{OH}^* + \text{H}^* + \text{CO}^*$ reaction.
Table 1. Adsorption energies (eV), vibrational frequencies (cm\(^{-1}\)) and structural parameters (Å) of reactants and products with and without co-adsorbed carbon monoxide. \(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>Adsorption site</th>
<th>(E_{\text{ads}}^e)</th>
<th>(E_{\text{ads}}^g)</th>
<th>Vibrational frequencies</th>
<th>(d_{\text{surf-mol}})</th>
<th>Bond length (^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{O}^+)</td>
<td>(t)</td>
<td>-0.36</td>
<td>-0.27</td>
<td>3723, 3612, 1558, 489, 427, 227, 172, 122, 84</td>
<td>(\text{H}_2\text{O}: 2.157)</td>
<td>O–H(_a): 0.979; O–H(_b): 0.978</td>
</tr>
<tr>
<td>(\text{OH}^+ + \text{H}^+)</td>
<td>(\text{OH}: f; \text{H}: f)</td>
<td>-6.23</td>
<td>-5.83</td>
<td>3712, 1220, 952, 776, 546, 502, 387, 290, 248</td>
<td>(\text{OH}: 1.950; \text{H}: 1.655)</td>
<td>O–H: 0.973</td>
</tr>
<tr>
<td>(\text{H}_2\text{O}^+ + \text{CO}^+)</td>
<td>(\text{H}_2\text{O}: t; \text{CO}: f)</td>
<td>-2.38</td>
<td>-2.32</td>
<td>3721, 3412, 1662, 1566, 737, 516, 379, 349, 322, 306, 226, 190, 149, 128, 76</td>
<td>(\text{H}_2\text{O}: 2.114; \text{CO}: 1.903)</td>
<td>O–H(_a): 0.990; O–H(_b): 0.975; C–O: 1.213</td>
</tr>
<tr>
<td>(\text{OH}^+ + \text{H}^+ + \text{CO}^+)</td>
<td>(\text{OH}: f; \text{H}: f; \text{CO}: f)</td>
<td>-7.99</td>
<td>-7.63</td>
<td>3704, 1761, 1253, 972, 740, 567, 520, 415, 395, 322, 299, 277, 246, 166, 122</td>
<td>(\text{OH}: 1.923; \text{H}: 1.646; \text{CO}: 1.872)</td>
<td>O–H(_a): 0.974; O–H(_b): 0.974; C–O: 1.195</td>
</tr>
</tbody>
</table>

* For the adsorption energies (\(E_{\text{ads}}\)), \("e"\) and \("g"\) denote the uncorrected and ZPVE-corrected values, respectively. \(^b\) Shortest distance between any atom of the adsorbate(s) and any metal atom on the surface; \(^c\) Letter “a” shows the O–H bond nearest the CO and “b” the other O–H bond.

The presence of the CO does not affect the preferred adsorption sites. The favored adsorption site for water is the top site (t) via the O atom and for carbon monoxide it is the hollow fcc site (f) via the C atom. The adsorption energy is \(-2.32\) eV \((-2.38\) eV without ZPVE correction). All of the products prefer the hollow fcc site (f), where the OH is adsorbed via the O atom and CO via the C atom. The adsorption energy is \(-7.63\) eV \((-7.99\) eV without ZPVE correction).

The calculations performed for the higher surface coverages yielded similar results to those presented above. For example, for 1/4 monolayer (only water) and 1/2 monolayer (co-adsorbed water and CO) coverages, the reactant adsorption energies are \(-0.20\) eV \((-0.26\) eV without ZPVE correction) and \(-2.43\) eV \((-2.35\) eV without ZPVE correction), respectively.

Although the presence of the CO does not affect the preferred adsorption site, it does affect the reactant geometry. In the absence of the CO the lengths of the O–H bonds in the water molecule are almost the same (0.98 Å) while, in the presence of CO, the O–H bond closest to the CO molecule is 0.015 Å longer than the other bond. This larger bond length is probably due to interactions between this H atom and the CO molecule (the distance between this H and the O on the CO is just 1.88 Å), although the charge density on this H atom is the same as the charge density on the other H atom. This is also reflected in the vibrational frequencies where the asymmetric stretching mode is lowered by 200 cm\(^{-1}\) (from 3612 to 3412 cm\(^{-1}\) in the absence and presence of CO, respectively). The presence of the CO does not have a significant effect on the OH product geometry or vibrational frequency.

The co-adsorbed CO also affects the distance between the reactant and products with the Ni surface (defined as the shortest distance between any atom of the adsorbate and any metal atom on the surface). The distance between the \(\text{H}_2\text{O}\) and the surface decreases from 2.157 Å to 2.114 Å when the CO is present, for OH the decrease is from 1.950 Å to 1.923 Å, and for H the decrease is from 1.655 Å to 1.646 Å. The reason that the presence of the CO molecule decreases the height of the reactant and products above the surface is probably due to electron transfer from the CO to the Ni surface. In the presence of the CO the total charge density on the uppermost Ni atoms is 0.63 e more than in the absence of the CO. This increases the interaction strengths (and hence decreases the bond lengths) between the surface and the
adsorbants, which is also seen by an increase in the charge density on the H$_2$O, OH and H adsorbants by 0.01, 0.04 and 0.03 e, respectively.

2.2. Transition States and Reaction Energies

Table 2 shows the data of the transition states together with reaction rate constants at 463 K, which is typical for low-temperature processes that include the WGS reaction [55]. The activation energy ($E_a$) without co-adsorbed CO is 0.75 eV (0.96 eV without ZPVE correction) and in the presence of CO it increases to 0.87 eV (1.09 eV without ZPVE correction), respectively. The activation energy in the absence of CO is in agreement with that obtained by Fajín et al. (0.71 eV). Similarly, the value determined in the presence of CO is similar to the value of 0.79 eV reported by Lin et al. The same trend is found for higher coverages. For the 1/4 and 1/2 monolayer surfaces the activation barrier in the absence of CO is 0.69 eV (0.87 eV without ZPVE correction) and in the presence of CO it is 1.18 eV (1.39 eV without ZPVE correction). Hence, the presence of CO increases the activation energy at both surface coverages.

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_a^0$</th>
<th>$E_a^0$</th>
<th>Vibrational modes</th>
<th>$k$</th>
<th>$E_{\text{react}}^0$</th>
<th>$E_{\text{react}}^0$</th>
<th>$d_{O-H}$</th>
<th>Imaginary frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O$^<em>$ → OH$^</em>$ + H$^*$</td>
<td>0.96</td>
<td>0.75</td>
<td>3653, 837, 748, 677, 432, 393, 167, 71</td>
<td>2.03×10$^4$</td>
<td>−0.30</td>
<td>−0.41</td>
<td>1.559</td>
<td>797</td>
</tr>
<tr>
<td>H$_2$O$^<em>$ + CO$^</em>$ → OH$^<em>$ + H$^</em>$ + CO$^*$</td>
<td>1.09</td>
<td>0.87</td>
<td>690, 465, 400, 377, 324, 1.76×10$^3$</td>
<td>−0.05</td>
<td>−0.17</td>
<td>1.560</td>
<td>817</td>
<td></td>
</tr>
</tbody>
</table>

* For the activation energies ($E_a$), "e" and "°" denote the uncorrected and ZPVE-corrected values, respectively.

The length of the breaking O–H bond is not significantly influenced by CO co-adsorption, and its (imaginary) vibrational frequency is increased by only 20 cm$^{-1}$. This means that the reaction barrier is slightly narrower in the presence of the CO. However, this effect is not as significant as it is for the water reactant, where the presence of the CO decreased the asymmetric vibrational mode frequency by 200 cm$^{-1}$.

Unlike the length and frequency of the breaking bond, the reaction rate constant changes considerably when CO is present, decreasing from 2.03 × 10$^4$ s$^{-1}$ to 1.76 × 10$^3$ s$^{-1}$. The rate constant in the absence of CO is smaller than the value of 7.1 × 10$^4$ s$^{-1}$ obtained by Fajín et al. [33]. This may be due to the convergence criteria, since repeating the above calculation, but with coarser convergence criteria of 10$^{-3}$ eV for the total energy and 10$^{-2}$ eV/Å for the forces acting on ions, yields the same result as that reported by Fajín et al. The reaction energy ($E_{\text{react}}$), which is the difference between the product and reactant energies, is significantly affected by the presence of co-adsorbed CO. In the absence of CO $E_{\text{react}} = −0.41$ eV (−0.30 eV without ZPVE correction) which is 0.24 eV more exothermic than the reaction energy in the presence of CO, which is −0.17 eV (−0.05 eV without ZPVE correction). The reaction energy calculated
in the absence of CO is similar to that obtained by Fajín et al. (−0.31 eV). Similarly, the calculated reaction energy in the presence of co-adsorbed CO is similar to the value of −0.11 eV obtained by Line et al. [33,50].

A comparison of the reaction profiles with and without adsorbed carbon monoxide is shown in Figure 4. As discussed above, the co-adsorbed CO increases the activation barrier by 0.12 eV and decreases the exothermicity by 0.24 eV. A possible reason for the larger activation energy is that the CO (and Ni surface) induces a larger change in the structure of the water molecule when going from reactant to transition state. To investigate these we performed single point energy calculations on the water molecule (in vacuum) in its reactant and transition state structures. It was seen that this does not explain the trends seen in Figure 4, since the energy of the water molecule in the transition state structure is lower than the energy in the reactant structure, and hence it is changes in the CO, Ni surface or interactions between the water-CO-Ni that lead to the increase in energy at the transition state. Similarly, calculations comparing the energies of the reactant water and product H and OH structures showed that this cannot explain the decrease in exothermicity in the presence of the CO. In fact, when comparing the H₂O and (H + OH) energies the reaction is endothermic when using the structures from the both systems (in the absence and presence of the CO).

Figure 4. Reaction profiles for the water dissociation with (dashed line) and without (solid line) co-adsorbed CO.

These calculations were repeated but where the CO molecule was included (together with the water molecule). This was done to ascertain whether it is changes in the CO molecule and/or interactions between the H₂O and CO that leads to an increase in the transition state energy compared to the energy of the reactant. Once again, the H₂O-CO energy (in the vacuum) of the transition state structure was lower than the energy of the reactant structure, and the reaction is more exothermic than that when using the structures from the system that does not contain CO (thus opposite to what is observed in Figure 4).

Hence, it is the interplay between all three components—the H₂O, CO and Ni surface—that leads to the reaction profiles seen in Figure 4. As discussed above, the presence of the CO on the surface leads to stronger interactions between the Ni surface and the H₂O reactant and H and OH products. The larger activation energy and decreased exothermicity indicates that the stability induced by the surface in the presence of CO is larger for the reactant than for the transition state and product structures.
Figure 5 shows the effect of temperature on the reaction rate constant. The data is also shown in its Arrhenius form in the inset to the figure. The difference in reaction rate constants in the absence and presence of CO increases with increasing temperature, showing that it becomes even more important to consider the effect of CO co-adsorption at higher temperatures.

**Figure 5.** Temperature dependence of the reaction rate constant for the water dissociation reaction with and without co-adsorbed carbon monoxide. The Arrhenius format of the data is shown in the inset.

3. Methods and Models

The calculations were performed with the Vienna *ab initio* simulation package (VASP) [56–59] using spin polarized DFT. The Perdew-Burke-Ernzerhof generalized gradient approach (GGA-PBE) [60] to the exchange-correlation potential was implemented and the projector-augmented wave method (PAW) [61,62] was applied to the basis set to account for the effect of the core electrons in the valence electron density. A 600-eV cutoff for the plane waves expansion was applied and a 4 × 4 × 1 Monkhorst-Pack grid of *k*-points [63] was used for the numerical integration in reciprocal space. As shown previously [50] smaller Brillouin zone (BZ) sampling intervals (5 × 5 × 1 and 6 × 6 × 1) and higher cutoff energies (700 and 800 eV) show insignificant differences in the energies of the optimized structures (less than 0.01 eV). Hence, the cutoff and Monkhorst-Pack grid used here yield converged results.

The surface orientation, as well as steps and defects on the surface, could affect its catalytic properties and reactions energies [14,64]. The face-centered cubic (fcc) nickel, Ni(111), is the most stable Ni surface and is therefore commonly used in computational studies of heterogeneous catalytic reactions [65–69]. This surface was also used in the present work, where periodic boundary conditions were imposed in two directions to model a semi-infinite crystal surface. Tests showed that a Ni(111) surface containing 4 × 4 unit cells in each layer, and with five layers that are separated by an equivalent volume of vacuum in the surface perpendicular direction, yield converged results in a computationally tractable time. The two bottom layers of the slab were fixed to maintain the bulk crystal structure, and the three upper layers were free to relax. This periodic box size, which yields a 1/16 monolayer coverage for the water in the absence of CO and a 1/8 monolayer for the co-adsorbed CO and water, prevents interactions between the surface atoms and adsorbates with their periodic images. Higher surface
coverages, including 1/4 and 1/2 monolayer, were also investigated to elucidate if the trends reported here are sensitive to the surface coverage.

The conjugate-gradient (CG) method was used to obtain the geometry optimized structures of the adsorbates on the surface. The convergence criteria were $10^{-6}$ eV for the total energy and $10^{-3}$ eV/Å for the forces acting on the ions.

Transition states were identified using an improved version of the nudged elastic band (NEB) method, called climbing-image NEB (CI-NEB) [70,71]. In this method, the lowest energy reactant and product configurations are selected as the initial and final states, and 6 images were placed along the minimum energy path (MEP). A $-0.5$ eV Å$^{-2}$ spring force constant between images was used. Due to computational constraints, a smaller set of $k$-points ($2 \times 2 \times 1$) and a lower energy cutoff (400 eV) was used to relax all the images until the maximum force acting on an atom was less than 0.01 eV. Single point energy calculations at the transition state using $4 \times 4 \times 1$ $k$-mesh and 600 eV cut off showed that the activation energy differs from that obtained with the less accurate settings by at most 0.02 eV.

Vibrational frequencies were calculated at all stationary points to ensure that they were minimum energy (zero imaginary frequencies) or transition states (one imaginary frequency) geometries, as well as to determine the zero point vibrational energies (ZPVEs) and partition functions. The frequencies were determined by diagonalizing a finite difference construction of the Hessian matrix using displacements of 0.01 Å (only the adsorbates were allowed to move).

The adsorption energies ($E_{\text{ads}}$) of the reactants and products were calculated from Equation (1).

$$E_{\text{ads}} = E_{\text{surf}} + \text{adsorbate} - E_{\text{surf}} - E_{\text{adsorbate}}$$  \hspace{1cm} (1)

where $E_{\text{surf}}$ is the total energy of the Ni(111) surface, $E_{\text{adsorbate}}$ is the total energy of the isolated, geometry optimized adsorbate(s) in the gas phase and $E_{\text{surf}} + \text{adsorbate}$ is the total energy of the surface-adsorbate(s) system. Results of $E_{\text{ads}}$ where ZPVE corrections are excluded ($E_{\text{ads}}^0$) and included ($E_{\text{ads}}$) are given below for the sake of completeness and to show the importance of this correction.

The water dissociation rate constant ($k$) was estimated using transition state theory [72], i.e., Equation (2).

$$k_{\text{TST}} = \left( \frac{k_B T}{h} \right) \left( \frac{q}{q^#} \right) e^{-E_a/k_B T}$$ \hspace{1cm} (2)

where $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, $h$ is Planck’s constant and $E_a$ is the activation energy from the ZPVE corrected energies. $q$ and $q^#$ are the partition functions for the reactant and the transition state respectively. Similarly to previous studies [14,33,73], the partition functions have been calculated assuming harmonic vibrations. Although this approximation may well affect the quantitative results presented here, it is not expected to affect the trends.

The effect of the CO on the reactant, transition state and product geometries was analyzed using the atomic charge densities. These calculations were performed using $2 \times 2$ unit cells in each layer, since these cells yield the same geometric and energetic trends as the larger unit cells. The charge density on each ion in the relaxed structure is calculated by integrating the valence charge density within the Wigner-Seitz spheres around each atom. This radius is selected such that the total volume over all atoms is approximately 100% and that the ratios of the atomic radii is equal to that of the ionic radii [74]. The present calculations use a $8 \times 8 \times 1$ $k$-point meshes and Wigner-Seitz radii equal to
1.4 Å for Ni, 1.29 Å for carbon, 1.11 Å for oxygen and 0.7 Å for hydrogen. Altering these radii by up to 10% does not change the trends reported here.

4. Conclusions

The effect of CO co-adsorption on water dissociation over the Ni(111) nickel surface has been studied using DFT calculations. The results show that the co-adsorption of CO alters the geometry of the adsorbed reactant water molecule. The O–H bond that is closest to the CO is lengthened and weakened. In addition, the distance between the reactants and products with the surface decreases in the presence of the co-adsorbed CO. These changes result in a dissociation energy that is 0.24 eV less exothermic in the presence of the CO.

The results also show that the activation energy for water dissociation increases by 0.12 eV in the presence of the co-adsorbed CO. In addition, the breaking O–H bond at the transition state has a slightly larger imaginary vibrational frequency in the presence of the co-adsorbed CO. These changes (including changes in the reactant geometries and vibrational frequencies) lead to a considerable decrease in the rate constant when CO is present. At typical low-temperature process conditions of 463 K, the rate constant in the presence of CO is approximately twelve times smaller than in the absence of CO, and this difference increases with increasing temperature. Hence, it is important to account for co-adsorbed CO when Ni-catalyzed water dissociation occurs in a CO-rich environment.

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Conflicts of Interest

The authors declare no conflict of interest.

References


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DT study of the adsorption and dissociation of water on Ni(111), Ni(110) and Ni(100) surfaces

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Water adsorption and dissociation on catalytic metal surfaces play a key role in a variety of industrial processes, and a detailed understanding of this process and how it is effected by the surface structure will assist in developing improved catalysts. Hence, a comparative study of the adsorption and dissociation of water on Ni(111), Ni(110) and Ni(100) surfaces, which is often used as catalyst, has been performed using density functional theory. The results show that the adsorption energies and dissociation rates depend on the surface structure. The adsorption energies for H2O and OH decrease in the order Ni(110) > Ni(100) > Ni(111), and for the O and H atoms the adsorption energies decrease in the order Ni(100) > Ni(111) > Ni(110). In addition, the splitting of water to OH and H has lower activation energies over less packed Ni(110) and Ni(100) surfaces compared to the highly packed Ni(111) surface. The subsequent splitting of the OH to O and H also has the lowest activation energy on the Ni(110) surface. At 463 K, which is typical for industrial processes that include the water gas shift reaction, the H2O splitting is approximately 6000 and 10 times faster on the Ni(110) surface compared to the Ni(111) and Ni(100) surfaces, respectively, and OH splitting is 200 and 3000 times faster, respectively. The complete water dissociation reaction rate decreases in the order Ni(110) > Ni(100) > Ni(111).

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1. Introduction

The interaction of water with solid surfaces is of great importance in many physical, chemical and biological processes. Water dissociation is believed to be one of the rate controlling elementary reaction steps in the water gas shift reaction (WGS; CO + H2O $\rightarrow$ CO2 + H2) and steam methane reforming (SMR; CH4 + H2O $\rightarrow$ CO + 3H2) [1,2] where nickel is frequently used as the catalyst. The WGS reaction is widely applied in the chemical industry to remove CO and to produce additional hydrogen. The dimers are bound to the nickel surface via both oxygen atoms, and the linear hydrogen bond axis is oriented parallel to the surface. The dimers are bound to the nickel surface via both oxygen atoms, and the linear hydrogen bond axis is oriented parallel to the surface. This orientation is believed to be one of the rate controlling elementary reaction steps in the water gas shift reaction (WGS; CO + H2O $\rightarrow$ CO2 + H2) and steam methane reforming (SMR; CH4 + H2O $\rightarrow$ CO + 3H2) [1,2] where nickel is frequently used as the catalyst. The WGS reaction is widely applied in the chemical industry to remove CO and to produce additional hydrogen. The dimers are bound to the nickel surface via both oxygen atoms, and the linear hydrogen bond axis is oriented parallel to the surface. This orientation is believed to be one of the rate controlling elementary reaction steps in the water gas shift reaction (WGS; CO + H2O $\rightarrow$ CO2 + H2) and steam methane reforming (SMR; CH4 + H2O $\rightarrow$ CO + 3H2) [1,2] where nickel is frequently used as the catalyst. The WGS reaction is widely applied in the chemical industry to remove CO and to produce additional hydrogen. The dimers are bound to the nickel surface via both oxygen atoms, and the linear hydrogen bond axis is oriented parallel to the surface. This orientation is believed to be one of the rate

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via its oxygen atom [17]. Pozzo et al. investigated water dissociation on Ni(111) and reported that water adsorbs on top nickel surface sites with a binding energy of 0.35 eV. Activation barriers of 0.89 and 0.97 eV have to be overcome to split the water into OH and H to split OH into O and H, respectively, on Ni(111) [18].

A DFT study of the WGS reaction and coke formation pathways on flat Ni(111) and stepped Ni(211) surfaces was performed by Catapan et al. This included the water dissociation elementary step. They obtained an activation barrier of 0.90 and 1.01 eV for water and OH splitting, respectively, on Ni(111) [19].

The present contribution extends previous investigations by using DFT to perform a comparative study of the adsorption and dissociation of water on Ni(111), Ni(110) and Ni(100) surfaces. This is the first time that these three different crystallographic orientations of the exposed surfaces have been studied using the same models and computational methods. If the crystallographic structure of the nickel catalyst affects the reactant, transition state or product relative energies or the vibrational frequencies, then the water adsorption strength and dissociation rate will depend on the type of nickel surface used as catalyst. These results are expected to aid in identifying which of the three crystallographic surfaces is the most efficient for water dissociation.

2. Methods and models

2.1. Calculated polarized DFT calculations were performed using the Vienna ab initio simulation package (VASP) [20–23]. The exchange-correlation functional with the generalized gradient approximation of Perdew, Burke and Ernzerh (GGA-PBE) [24] was combined with the projector-augmented wave method (PAW) [25,26] to solve the Kohn-Sham equations. The Kohn-Sham orbitals were expanded in a plane-wave basis set using a 400 eV kinetic energy cut off, and a 4 × 4 × 1 Monkhorst-Pack grid of k-points [27] was used for the numerical integration in reciprocal space. Test calculations showed that larger cut off and finer k-meshes yielded the same trends reported below. Also, for the density of states calculations, a dense 41 × 41 1 k-point grid was employed. A 0.1 eV Fermi smearing was used and the convergence criteria for the geometry optimizations were 10−6 eV for the total energy and 10−3 eVÅ−1 for the forces acting on the ions. The conjugate-gradient (CG) method was used for the geometry optimizations.

Previous studies have shown that the catalytic properties and reaction energies are affected by the surface orientation, steps and defects [28,29] and that nickel particles grown on oxide or graphite substrates have polyhedral shapes exhibiting (111), (110) and (100) facets [30]. These nickel facets were, therefore, used to study the water adsorption and dissociation.

Surfaces were constructed using 2 × 2 unit cells with four layers, and periodic boundary conditions in two directions to model a semi-infinite crystal surface. The two upper layers were free to relax while the bottom half of the slab was fixed to maintain the bulk crystal structure. This periodic box size, which corresponds to a 1/4 and 1/2 monolayer (ML) coverage when there are one and two adsorbates, respectively, has been widely used in previous investigations of adsorption on transition metal surfaces [31–33] and yields converged results in a computationally tractable time. Lower surface coverages were also examined and yielded the same trends reported below [34].

Transition states were identified using the climbing image - nudged elastic band (CI-NEB) method [35,36], where the lowest energy reactant and product configurations are selected as the initial and final states. Six images were placed along the minimum energy path (MEP) and a −0.5 eVÅ−1 spring force constant between images was used to relax all of the images until the maximum force acting on each atom was less than 0.1 eVÅ−1. Calculations using a 0.01 eVÅ−1 convergence criteria showed that the activation energy differs from that obtained with 0.1 eVÅ−1 by at most 0.2 meV.

Vibrational frequencies were calculated at all stationary points (reactants, products and transition states) by diagonalizing a finite difference construction of the Hessian matrix using displacements of 0.01 Å and where only the adsorbates were allowed to move. These frequencies were used to ensure that the structures were minimum energy structures (zero imaginary frequencies) or transition states (one imaginary frequency) and to calculate the vibrational partition functions and zero point vibrational energies (ZPVEs).

The adsorption energies (Eads) of the reactants and products were calculated using Eq. (1).

\[ E_{ads} = E_{surf + adsorbate} - E_{surf} - E_{adsorbate} \]  

where \( E_{surf + adsorbate} \) is the total energy of the surface-adsorbate(s) system, \( E_{surf} \) is the total energy of the surface and \( E_{adsorbate} \) is the total energy of the isolated, geometry optimized adsorbate(s) in the gas phase. Data for the uncorrected and ZPVE corrected adsorption energies are presented to show the effect of this correction. The dissociation rate constants (k) were estimated from transition state theory [37] using Eq. (2).

\[ k = \left( \frac{k_B T}{h} \right) \left( \frac{q^+ q^-}{q^+ q^-} \right) e^{\frac{E_{ads}}{k_B T}} \]  

where \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature and \( h \) is Planck’s constant. \( q^+ \) and \( q^- \) are the partition functions for the reactant and the transition state, respectively, and \( E_{ads} \) is the ZPVE corrected activation energy. The partition functions have been estimated assuming harmonic vibrations. Although this approximation may well affect the quantitative results presented here, it is not expected to affect the trends [15,29,38].

2.2. Adsorption sites

As shown in the left panel of Fig. 1, there are four high symmetry adsorption sites on the Ni(111) crystal surface. The top site is above the uppermost Ni surface atom and is labeled A, the hcp 3-fold hollow site (where the central metallic atom in this site is in the second surface layer) is labeled C, the fcc 3-fold hollow site (where the central metallic atom is in the third surface layer) is labeled C′ and the 2-fold bridge site between two neighboring atoms is labeled B. There are five high symmetry adsorption sites on the Ni(110) surface. These are the top site labeled A, a 2-fold long bridge site labeled E, a 2-fold short bridge site labeled F, a rectangular 4-fold hollow site labeled D and a quasi 3-fold hollow site labeled G (which is located in the middle of the short bridge and the 4-fold sites). In addition to the top and bridge sites labeled A and B, the Ni(100) crystal surface has a square 4-fold hollow adsorption site labeled D′.

2.3. Kinetic model

The ODE45 solver in the MATLAB R2013a simulation package [39] was employed to solve the following ordinary differential equations (ODEs):

\[ \frac{d[H_2O]}{dt} = -k_1[H_2O] \]  

\[ \frac{d[OH]}{dt} = k_1[H_2O] - k_2[OH] \]  

\[ \frac{d[H]}{dt} = k_1[H_2O] + k_2[OH] \]  

\[ \frac{d[O]}{dt} = k_2[OH] \]
3. Results and discussion

3.1. Adsorption energies

Geometry optimizations were performed for all adsorption sites shown in Fig. 1 and for different orientations of the adsorbates. The lowest energy structures were then selected for subsequent investigations of the reaction mechanism and rates. Details of the lowest energy structures of the individual chemical species that are involved in H₂O dissociation are presented in Table 1, together with results from previous studies. The preferred adsorption site for water is the top site (A) for all surfaces, which is in agreement with previous results (references given in the table). The strongest adsorption is −0.39 eV (−0.47 eV without ZPVE) on the Ni(110) surface, compared to −0.27 eV (−0.34 eV without ZPVE) for Ni(100) and −0.20 eV (−0.26 eV without ZPVE) for Ni(111). The two O–H bonds have the same lengths on the Ni(111) and Ni(100) surfaces, whereas one of the O–H bonds (the breaking bond) is longer than the other bond by about 0.01 Å on the Ni(110) surface. The surface-adsorbate distance, defined as the distance between any atom of the adsorbate and the nearest Ni atom, is the shortest on the Ni(111) surface (which is also the surface that has the strongest adsorption). The O–H bond lengths and H–O–H angle for the isolated water molecule are 0.973 Å and 104.2°, respectively, which are smaller compared to the adsorbed water on all surfaces. Hence, the catalyst surfaces increase the bond lengths and bond angle.

Fajín et al. reported water adsorption energies of −0.32 and −0.54 eV, surface-adsorbate distances of 2.23 and 2.09 Å, and O–H bond lengths of 0.98 and 0.98 Å for Ni(111) and Ni(110), respectively [15]. Seenivasan et al. obtained adsorption energies of −0.17 and −0.26 eV, and O–H bond lengths of 0.98 and 0.98 Å for Ni(111) and Ni(100), respectively [42]. They also obtained the heights of H₂O oxygen atoms above the Ni(111) and Ni(100) surfaces, respectively, as 2.33 and 2.30 Å.

Table 1

<table>
<thead>
<tr>
<th>Surface</th>
<th>Adsorption site</th>
<th>E_ads (eV)</th>
<th>E_zpe (eV)</th>
<th>d_adsorbate (Å)</th>
<th>Bond length (Å)</th>
<th>Eads-dsurf-ads (eV)</th>
<th>Previous results for E_ads (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>Ni(111)</td>
<td>A</td>
<td>−0.26</td>
<td>−0.20</td>
<td>2.225</td>
<td>O–H: 0.982, O–H₂: 0.982</td>
<td>−0.25⁵, −0.32⁵, −0.47², −0.17⁷</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>A</td>
<td>−0.47</td>
<td>−0.39</td>
<td>2.007</td>
<td>O–H: 0.979, O–H₂: 0.990</td>
<td>−0.54⁴, −0.26⁰</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>A</td>
<td>−0.34</td>
<td>−0.27</td>
<td>2.155</td>
<td>O–H: 0.982, O–H₂: 0.982</td>
<td>−0.41³, −0.34³, −0.30⁵, −0.33¹⁷</td>
</tr>
<tr>
<td>OH</td>
<td>Ni(111)</td>
<td>C</td>
<td>3.41</td>
<td>3.08</td>
<td>1.976</td>
<td>O–H₂: 0.974</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>F</td>
<td>−3.80</td>
<td>−3.44</td>
<td>1.918</td>
<td>O–H₂: 0.978</td>
<td>−3.37³, −3.26³, −3.57³</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>D¹</td>
<td>−3.62</td>
<td>−3.27</td>
<td>2.102</td>
<td>O–H₂: 0.978</td>
<td>−3.37³, −3.26³, −3.57³</td>
</tr>
<tr>
<td>O</td>
<td>Ni(111)</td>
<td>C</td>
<td>3.59</td>
<td>3.31</td>
<td>1.836</td>
<td></td>
<td>−5.50³, −5.66³, −4.81³, −5.14³</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>E</td>
<td>−5.04</td>
<td>−4.98</td>
<td>1.897</td>
<td></td>
<td>−5.49⁶</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>D²</td>
<td>−5.69</td>
<td>−5.63</td>
<td>1.950</td>
<td></td>
<td>−5.46³</td>
</tr>
<tr>
<td>H</td>
<td>Ni(111)</td>
<td>C¹</td>
<td>−2.84</td>
<td>−2.66</td>
<td>1.707</td>
<td></td>
<td>−2.78³, −2.77³, −2.80³, −0.60³, −0.49³</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>G</td>
<td>−2.68</td>
<td>−2.51</td>
<td>1.699</td>
<td></td>
<td>−0.49³, −0.37³</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>D²</td>
<td>−2.82</td>
<td>−2.70</td>
<td>1.838</td>
<td></td>
<td>−2.83³, −2.64³, −2.80³, −0.57³, −0.59³</td>
</tr>
</tbody>
</table>

*For the adsorption energies (E_ads), „t“ and „zpe“ denote the uncorrected and ZPVE-corrected values, respectively. "Shortest distance between any atom of the adsorbate(s) and any metal atom on the surface. "O–H₂ is the bond which is broken during the reaction. "Reference [18] (GGA-PBE calculations using a 2 × 2 unit cell and three layer slab). "Reference [15] (GGA-PW91 calculations using a 2 × 2 unit cell and four layer slab). "Reference [19] (GGA-PBE calculations using a 2 × 2 unit cell and four layer slab). "Reference [40] (GGA-PBE calculations using a 3 × 2 unit cell and three layer slab). "Reference [41] (GGA-RPBE calculations using a 2 × 2 unit cell and three layer slab). "Reference [42] (GGA-PBE calculations using a 2 × 2 unit cell and four layer slab). "Reference [43] (GGA-PW91 calculations using a 2 × 2 unit cell and four layer slab). "Reference [44] (GGA-PW91 calculations using a 2 × 2 unit cell and four layer slab).
2.20 Å, which can be compared to the values obtained in the present studies of 2.222 and 2.146 Å (the height above the Ni(110) surface is 1.996 Å). Pozzo et al. reported an H–O–H angle of 104.9 degrees on Ni(111) [18]. No previous results for the H–O–H angle have been reported for the Ni(110) and Ni(100) surfaces. Hence, previous results also show that the adsorption energy is weakest on the Ni(111) surface and that this is associated with the longest surface-adsorbate distance. The OH adsorption energy follows the same trend as that discussed above for water, although the preferred adsorption sites are F for Ni(110), D′ for Ni(100) and C′ for Ni(111). The strongest adsorption is on the Ni(110) surface and is −3.44 eV (−3.80 eV without ZPVE). This can be compared to 3.27 eV (−3.62 eV without ZPVE) for Ni(100) and −3.08 eV (−3.41 eV without ZPVE) for Ni(111). As for H2O, the surface-adsorbate distance for OH is the shortest when the binding energy is strongest. The O–H bond length is similar on all three surfaces, and is shorter than the bond length of O–H in vacuum, which is 0.988 Å. Hence, interaction with the Ni surfaces decreases the O–H bond length.

OH adsorption energies obtained in previous studies are listed in Table 1. For example, Zhou et al. obtained an adsorption energy of −3.37 eV with a surface-adsorbate distance of 2.09 Å on the Ni(100) surface [40]. Seenivasan et al. calculated adsorption energies of −3.31 and −3.57 eV, and O–H bond lengths of 0.97 and 0.98 Å on the Ni(111) and Ni(100) surfaces, respectively [42]. Hence the results obtained in the present work are in agreement with (and are spanned by) previously calculated data when available. Seenivasan et al. also obtain heights of the OH oxygen atom above the Ni(111) and Ni(100) surfaces, respectively, as 1.36 and 1.17 Å, which can be compared to the values obtained in this work of 1.355 and 1.123 Å (the value obtained for the Ni(110) surface is 1.457 Å).

The most stable adsorption sites for oxygen are C′ on the Ni(111) surface, E on Ni(110) and D′ on Ni(100) with binding energies of −5.31 eV (−5.39 eV without ZPVE), −4.98 eV (−5.04 eV without ZPVE) and −5.63 eV (−5.69 eV without ZPVE), respectively. The surface-adsorbate distances are 1.836, 1.897 and 1.950 Å for these three surfaces. Hence, in contrast to water and OH, oxygen does not have the strongest bonding to the Ni(110) surface and the surface-adsorbate distance does not decrease with increasing adhesion strength. However, the results presented here are in agreement with those obtained previously. For example, Fajín et al. obtained adsorption energies of −5.60 and −5.49 eV with surface-adsorbate distances of 2.13 and 1.82 Å for Ni(111) and Ni(110), respectively [15]. Hence, although they obtain larger bonding energies than those obtained in the present work (they used the PW91 method), they also obtain stronger adhesion on Ni(111) at the same time as the surface-adsorbate distance is longer than on Ni(110). Blaylock et al. reported adsorption energies of −4.81 and −5.46 eV for Ni(111) and Ni(100), respectively [41], which is in agreement with the trends seen in the present work. Surface-adsorbate distances on the Ni(100) surface have not been reported previously.

The preferred adsorption sites for hydrogen are C′ on the Ni(111) surface, G on Ni(110) and D′ on Ni(100) with binding energies of −2.66 eV (−2.84 eV without ZPVE), −2.51 eV (−2.68 eV without ZPVE) and −2.70 eV (−2.82 eV without ZPVE), respectively. The surface-adsorbate distances are 1.707, 1.669 and 1.838 Å for these three surfaces. Hence, similarly to oxygen, hydrogen has largest adhesion to the Ni(100) surface at the same time that the surface-adsorbate distance is longest on this surface. These results are similar to those obtained by Pozzo et al. and Cataoan et al. who reported −2.87 eV and −2.77 eV, respectively, for the adsorption energy of atomic hydrogen on the Ni(111) surface [18,19]. Zhou et al. and Seenivasan et al. obtained adsorption energies of −2.83 eV and −2.80 eV, respectively, for the Ni(100) surface [40,42]. Kresse et al. reported adsorption energies of −0.6, −0.45 and −0.57 eV for Ni(111), Ni(110) and Ni(100), respectively [43]. Bhatia et al. also reported adsorption energies of −0.49, −0.37 and −0.55 eV with a Ni–H distance of 1.71, 1.69 and 1.84 Å for Ni(111), Ni(110) and Ni(100) surfaces, respectively [44]. The adsorption energies reported by Kresse et al. and Bhatia et al. are hence far lower than those reported by others (although the trends are similar), and the difference is probably due to the fact that they used half of the hydrogen molecule (H2) energy as the energy of the isolated adsorbate (E_{adsorbate} in Eq. (1)). In this work, the energy calculated for isolated H2 is −6.76 eV and for atomic H it is −1.12 eV. The data in Table 1 are for single adsorbates on the Ni surfaces. Water splitting (H2O → OH + H) and OH splitting (OH → O + H) yield two product species that are initially near to each other on the Ni surface. The initial geometries for the optimizations when there are two adsorbates were obtained by placing them in their minimum energy sites (for the isolated adsorbates) and where these are neighboring sites. The co-adsorption sites obtained from the geometry optimizations, the adsorption energies and the molecular structures are given in Table 2. In all cases the co-adsorption sites are the same as those found for the isolated adsorbates, except for oxygen on the Ni(110) surface where attraction to the hydrogen atom shifts the oxygen from the E to the G site.

The co-adsorption energies for the water splitting products are −5.52 eV (−5.83 eV without ZPVE) on the Ni(111) surface, −6.09 eV (−6.50 eV without ZPVE) on Ni(110) and −5.80 eV (−6.16 eV without ZPVE) on Ni(100). The co-adsorption energy is therefore highest on the Ni(110) surface, which was also seen for the OH adsorbate. The surface-adsorbate distance is similar for co-adsorbed OH and isolated adsorbed OH. In contrast, co-adsorbed H is about 0.05 Å closer to both the Ni(111) and Ni(110) surfaces, and further away from the Ni(110) surface by about 0.05 Å. The O–H bond length was not altered by the co-adsorption. Co-adsorption data for the products of water splitting have not been reported previously, and hence comparison with other studies is not possible.

The co-adsorption energies for the OH splitting products are −7.63 eV (−7.91 eV without ZPVE) on the Ni(111) surface, −7.84 eV (−8.11 eV without ZPVE) on the Ni(110) surface and −8.01 eV (−8.21 eV without ZPVE) on the Ni(100) surface. The co-adsorption energy is therefore highest on the Ni(100) surface, which was also seen for the isolated O and H adsorbates. The surface-adsorbate distance is very similar for single and co-adsorbed oxygen on Ni(111) and Ni(100), and the co-adsorbed oxygen is about 0.06 Å closer to the Ni(110) surface compared to single adsorbed oxygen. In contrast, co-adsorbed hydrogen is closer to the surface in all cases. Co-adsorption data for the products of OH splitting have not been reported previously.

3.2. Transition states and reaction energies

3.2.1. H2O splitting

Details of the water splitting transition states and reaction rate constants are presented in Table 3, together with results from previous studies. The geometries of the reactants, transition states and products are shown in Fig. 2. The rate constants are calculated at 463 K, which is typical for low-temperature WGS processes that include water dissoociation [45]. The activation energies are 0.69 eV (0.87 eV without ZPVE), 0.38 eV (0.60 eV without ZPVE) and 0.45 eV (0.66 eV without ZPVE) for Ni(111), Ni(110) and Ni(100), respectively. The activation barriers are in agreement with those obtained by Fajín et al., i.e., 0.71 eV for Ni(111) and 0.39 eV for Ni(110) [15]. Seenivasan et al. reported activation barriers of 0.79 and 0.74 eV for Ni(111) and Ni(100), respectively [42]. The latter energy differs from our result, which is in better agreement with the 0.40 eV obtained by Blaylock et al. [41]. Also, in recent studies of water splitting over metal surfaces, Fajín et al. proposed that the activation energies for water splitting can be obtained from the co-adsorption energies of OH and H when gaseous H2O is the reference (Eq. (3) in Ref. [46]). The calculations presented here yield values of these co-adsorption energies of −0.38 eV for Ni(111), −0.96 eV for Ni(110) and −0.66 eV for Ni(100). Using the method proposed by Fajín et al., these yield activation energies of 0.63, 0.38 and 0.51 eV for
Ni(111), Ni(110) and Ni(100), respectively, which agree very well with the energies calculated in the present study, i.e., 0.69, 0.38 and 0.45 eV, respectively. Hence, similarly to the trends seen in previous studies, the activation energy for water splitting is lowest on the Ni(111) surface and largest on the Ni(111) surface.

These results are also supported by experimental observations. Since the calculated water splitting barrier for the Ni(111) surface is larger than the water desorption energy, it is expected that water will desorb intact without proceeding to OH + H species. This is in agreement with the observation that a water monolayer desorbs when heating this surface to 165 K, without evidence that water splitting products are formed [47,48]. The calculated adsorption energy for the Ni(110) surface is larger than that for the Ni(111) surface, which is in agreement with the observation that a water monolayer remains adsorbed on the Ni(110) surface at temperatures larger than 165 K [47]. In addition, the water splitting barrier on the Ni(110) surface is lower than the desorption energy, which is consistent with the observation that the OH splitting product is observed at temperatures larger than 200 K [47]. In addition, Benndorf and Masey used a combination of experimental methods (electron stimulated desorption ion angular distribution, thermal desorption spectroscopy and low energy electron diffraction) to estimate an energy barrier of 0.5 eV for O–H bond breakage on clean Ni(110), which is close to the barrier calculated in this work [49].

The reaction rate constants are strongly influenced by the surface structure, and at 463 K they decrease from 7.36 × 10^7 s^-1 on Ni(111) to 7.62 × 10^6 s^-1 on Ni(100) and to 1.23 × 10^6 s^-1 on Ni(111). The values are comparable to 7.4 × 10^6 s^-1 for Ni(111) and 1.8 × 10^5 s^-1 for Ni(100) obtained by Fajín et al. [15]. The small deviations are probably due to differences in the convergence criteria, since repeating the calculation but with coarser convergence criteria of 10^-5 eV for the total energy and 10^-2 eV Å^-1 for the forces acting on ions yielded the same results as those reported by Fajín et al. The reason for this is that the difference in convergence criteria results in slightly different values for the frequencies and for the activation energies, and hence in the rate constants calculated from Eq. (2). Rate constants of water splitting on the Ni(100) surface have not previously been reported, and hence comparison cannot be made for this surface.

The reaction energies are the differences between the ZPVE-corrected product and reactant energies. The reaction is exothermic on all surfaces, with reaction energies of –0.18, –0.57 and –0.39 eV for Ni(111), Ni(110) and Ni(100), respectively. The most exothermic reaction occurs on Ni(110) which is 0.18 eV and 0.39 eV more exothermic than the reaction energy on Ni(100) and Ni(111), respectively.

### Table 2

<table>
<thead>
<tr>
<th>Surface</th>
<th>Adsorption site</th>
<th>E_{ads}</th>
<th>E_{surf-ads}</th>
<th>d_{surf-ads}</th>
<th>Bond length</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + H</td>
<td>Ni(111)</td>
<td>O: H', H: G'</td>
<td>-5.52</td>
<td>-5.52</td>
<td>OH: 1.794, H: 1.660</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>O: H, H: G</td>
<td>-5.60</td>
<td>-5.60</td>
<td>OH: 1.918, H: 1.753</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>O: H', H: D'</td>
<td>-5.80</td>
<td>-5.80</td>
<td>OH: 2.104, H: 1.789</td>
</tr>
<tr>
<td>O + H</td>
<td>Ni(111)</td>
<td>O: H', H: C'</td>
<td>-7.91</td>
<td>-7.63</td>
<td>O: 1.835, H: 1.660</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>O: H, H: G</td>
<td>-8.11</td>
<td>-7.64</td>
<td>O: 1.835, H: 1.688</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>O: H', H: D'</td>
<td>-8.21</td>
<td>-8.01</td>
<td>O: 1.948, H: 1.786</td>
</tr>
</tbody>
</table>

*For the adsorption energies (E_{ads}), *\(^{-}\)* and *\(^{+}\)* denote the uncorrected and ZPVE-corrected values, respectively. *\(^{-}\)* Shortest distance between any atom of the adsorbate(s) and any metal atom on the surface.

### Table 3

| H_2O splitting activation energies (eV), reaction rate constant at 463 K (s^-1), reaction energy (eV), length of the breaking OH bond at the transition state (Å) and its imaginary frequency (cm^-1) and structural parameters (Å and degrees).* |
|---------|----------|-------------|-------------|-------------|-------------|
| Surface | E_k | k | E_{react} | d_{O–H} | Imaginary frequency | d_{Ni–O} | d_{Ni–H} | \(\theta_{O–H}\) |
|Ni(111)  |
| This work | 0.69  | 1.23 \times 10^4 | -0.18 | 1.538 | 899 | 1.937 | 1.764 | 104.7 |
| Previous results | 0.89, 0.71, 0.90, 0.79  | 7.4 \times 10^4 | -0.37, -0.28 | 1.557, 1.556, 1.486 | 747, 748, 989 | 1.88 | 1.14 | 120.9, 103.6 |
|Ni(110)  |
| This work | 0.38  | 7.36 \times 10^4 | -0.57 | 1.334 | 1285 | 2.016 | 2.007 | 121.0 |
| Previous results | 0.39  | 1.8 \times 10^4 | -0.52 | 1.348 | 1273 | - | - | - |
|Ni(100)  |
| This work | 0.45  | 7.62 \times 10^4 | -0.39 | 1.340 | 1034 | 2.001 | 1.706 | 122.1 |
| Previous results | 0.40, 0.74  | - | -0.49 | 1.53 | 1068 | 1.93 | 1.17 | 119.8 |

i.e., $-0.52 \text{ eV}$ for Ni(110) and $-0.37 \text{ eV}$ for Ni(111) \cite{15} and by Blaylock et al., i.e., $-0.28 \text{ eV}$ for Ni(111) and $-0.49 \text{ eV}$ for Ni(100) \cite{41}.

### 3.2.2. OH splitting

Table 4 shows the data of the transition states and reaction rate constants for the OH splitting reaction. The geometries of the reactants, transition states and products are shown in Fig. 3. Similarly to the water splitting reaction, the rate constants are calculated at 463 K. The activation energies are $0.80 \text{ eV}$ (0.98 eV without ZPVE), $0.61 \text{ eV}$ (0.75 eV without ZPVE) and $0.89 \text{ eV}$ (1.06 eV without ZPVE) for Ni(111), Ni(110) and Ni(100), respectively. The activation barriers of OH splitting are higher compared to those of H$_2$O splitting. This is consistent with other DFT calculations. For example, Catapan et al. found a barrier of $1.01 \text{ eV}$ for OH splitting on Ni(111) which is higher than their $0.11 \text{ eV}$ barrier for H$_2$O splitting \cite{19}. Pozzo et al. obtained a barrier of $0.97 \text{ eV}$ for OH splitting, which is $0.08 \text{ eV}$ higher than that for H$_2$O splitting on the Ni(111) surface \cite{18,19}. Blaylock et al. reported activation barriers for OH splitting of $0.85$ and $1.18 \text{ eV}$ for Ni(111) and Ni(100), respectively \cite{41}, which is also the same trend as that obtained here. No results have previously been reported for Ni(110).

The breaking O–H bond is longest on the Ni(110) surface ($2.627 \text{ Å}$) compared to $1.548 \text{ Å}$ on Ni(100) and $1.340 \text{ Å}$ on Ni(111). As discussed previously, this is consistent with the lower imaginary vibrational frequency of about $700 \text{ cm}^{-1}$ and $500 \text{ cm}^{-1}$ of the O–H bond on the Ni(110) surface compared to the Ni(111) and Ni(100) surfaces, respectively. These results agree with those obtained by Catapan et al., who obtained a breaking O–H bond length of $1.374 \text{ Å}$ and an imaginary frequency of $1146 \text{ cm}^{-1}$ on the Ni(111) surface \cite{19}. Bond lengths and imaginary frequencies have not previously been reported for the two other surfaces. The nickel-hydrogen and nickel-oxygen distances decrease in the order Ni(111) > Ni(100) > Ni(110). Hence, the smallest activation energy corresponds to the structures where the O–H bond is longest and the O and H atoms of the transition state structure are closest to the surface.

The reaction rate constants are significantly affected by the surface structures, decreasing from $1.43 \times 10^6 \text{ s}^{-1}$ on Ni(110) to $1.14 \times 10^5 \text{ s}^{-1}$ on Ni(111) and to $1.26 \times 10^3 \text{ s}^{-1}$ on Ni(100). Similarly to water splitting, the reaction is fastest over Ni(110). Unlike H$_2$O splitting, the reaction is faster on Ni(111) than Ni(100). OH splitting is exothermic on both Ni(111) and Ni(100), with reaction energies of $-0.03$ and $-0.21 \text{ eV}$, respectively, while it is endothermic on Ni(110) with a

### Table 4

<table>
<thead>
<tr>
<th>Surface</th>
<th>$E_a^*$ (eV)</th>
<th>Reaction constant $k$ ($s^{-1}$)</th>
<th>$E_{\text{react}}^*$ (eV)</th>
<th>$d_{\text{O-H}}$ (Å)</th>
<th>Imaginary frequency (cm$^{-1}$)</th>
<th>$d_{\text{Ni-O}}$ (Å)</th>
<th>$d_{\text{Ni-H}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)</td>
<td>0.80</td>
<td>$1.14 \times 10^6$</td>
<td>$-0.03$</td>
<td>1.340</td>
<td>1199</td>
<td>1.930</td>
<td>1.777</td>
</tr>
<tr>
<td>Ni(110)</td>
<td>0.97$^d$, 1.01$^e$, 0.85$^f$</td>
<td>$1.43 \times 10^6$</td>
<td>$-0.20^d$</td>
<td>1.374$^e$</td>
<td>1146$^e$</td>
<td>1.759</td>
<td>1.614</td>
</tr>
<tr>
<td>Ni(100)</td>
<td>0.61</td>
<td>$1.26 \times 10^5$</td>
<td>$-0.21$</td>
<td>1.548</td>
<td>966</td>
<td>1.815</td>
<td>1.684</td>
</tr>
</tbody>
</table>

$^a$ Energies are the ZPVE-corrected values.$^b$ Shortest distance between oxygen of the adsorbate and any metal atom on the surface.$^c$ Shortest distance between hydrogen of the O–H breaking bond and any metal atom on the surface.$^d$ Reference \cite{18} (GGA-PBE calculations using a 2 × 2 unit cell and three layer slab).$^e$ Reference \cite{19} (GGA-PBE calculations using a 2 × 2 unit cell and four layer slab).$^f$ Reference \cite{41} (GGA-RPBE calculations using a 2 × 2 unit cell and three layer slab).
reaction energy of 0.13 eV. Capatan et al. obtained a reaction energy of 
\(-0.20\) eV on Ni(111) and Blaylock et al. obtained \(-0.31\) eV on Ni(100) \[19,41\] which, in agreement with the results presented here, show exothermic reactions on these surfaces.

3.3. Comparison between adsorption energies and reaction barriers

For any given metal surface, adsorbates typically bind more strongly 
to high symmetry sites than to low symmetry sites, and to atoms with 
low coordination numbers rather than high coordination numbers 
\[53–55\]. The coordination number of surface metal atoms is seven, 
eight and nine for Ni(110), Ni(100) and Ni(111), respectively. Hence, 
in agreement with this typical behavior, water and OH have highest 
adsorption energies on the less packed Ni(110) and Ni(100) surfaces 
compared to the highly packed Ni(111). The projected density of states 
(PDOS) of the metallic Ni d-band can also be used to explain the physi-
cal origin of the difference in catalytic activity for the different surfaces 
\[31,55,56\]. All of the adsorbates studied here are more negatively 
charged than when they are in vacuum, and this extra electron density 
is assumed to come from the frontier d-orbitals of the metal surface. 

Fig. 4 shows that the intensities of the occupied orbitals at the Fermi 
level are 2.7, 2.2 and 2.0 states/eV for Ni(110), Ni(100) and Ni(111), re-
spectively. Hence, the Ni(110) surface can donate more electron density 
and, in agreement with this, the adsorption energies of water and OH 
decrease in the order Ni(110) > Ni(100) > Ni(111). However, for the 
O and H atomic adsorbates and the co-adsorbed O and H, the adsorption 
energies decrease in the order Ni(100) > Ni(111) > Ni(110). In the case 
of hydrogen, this is consistent with Wang et al. who reported adsorption 
energies of \(-2.81\) eV for Ni(100) and \(-2.77\) eV for Ni(111) \[57\]. Fajín 
et al. also found the same trends to those obtained here, and reported 
adsorption energies for atomic oxygen of \(-5.49\) eV on Ni(110) and 
\(-5.60\) eV on Ni(111) \[15\].

The activation energy of a reaction is determined by its mechanism 
(i.e., the reaction path on the potential surface), which is, in turn, influ-
enced by the electronic and crystal structure of the catalyst surface. The 
average energy of the d-band, called the d-band center, is an important 
parameter which is used to determine the distribution of surface’s elec-
tronic energy levels \[56,58\]. It shows the ability to eject an electron from 
the d-band of the metal to the adsorbate. Generally, the surface is more 
reactive when the d-band center is closer to the Fermi level \[56,58\]. The 
calculated d-band centers are at \(-1.75\), \(-1.98\) and \(-2.08\) eV for the 
Ni(110), Ni(100) and Ni(111) surfaces, respectively. The reaction barrier 
for the H\(_2\)O and OH splitting on the three surfaces is the lowest for
Ni(110), which has a d-band center that is closer to the Fermi level by about 0.33 eV and 0.23 eV compared to the Ni(100) and Ni(111) surfaces, respectively.

### 3.4. Reaction kinetics

The reaction profiles for the entire water dissociation process are compared in Fig. 5. It is evident that the activation energy for H$_2$O splitting on Ni(110) is 0.07 and 0.31 eV lower than on the Ni(100) and Ni(111) surfaces, respectively. This leads to a reaction rate constant at 463 K that is 10 and 6 × 10$^3$ times larger on the Ni(110) surface than on the Ni(100) and Ni(111) surfaces, respectively. The same effect is seen for OH splitting where the reaction rate constant on the Ni(110) surface is 10$^2$ and 10$^3$ times larger than on the Ni(111) and Ni(100) surfaces, respectively.

In fact, as shown in Fig. 6, the difference in reaction rate constants increases with increasing temperature. This shows that it becomes even more important to consider the effect of surface configuration at elevated temperatures.

Fig. 7 shows the time dependence of the relative concentrations of reactant, intermediate and products for water dissociation. The temperature is 463 K and it is assumed that the initial concentration of adsorbed water is 1 (arbitrary units of concentration). For the sake of clarity it is also assumed that the reaction is much faster than the rate of adsorbing new water molecules. Hence, the concentration of adsorbed water decreases until it reaches zero. Including the adsorption and desorption rates of reactants, intermediates and products, as well as the temperature dependence of these processes, is left for future work.

It is evident that consumption of the reactant (H$_2$O) is fastest on Ni(110) and follows the order Ni(110) > Ni(100) > Ni(111). At the same time more intermediate, OH, is produced on the Ni(110) surface and subsequent conversion to O and H products is also fastest on this surface. Production of H and O is consequently faster on the Ni(110)
larger on the Ni(110) surface, and the difference in rate constants on this surface and the other two surfaces increases with increasing temperature. At 463 K, which is typical for industrial processes that involve the WGS reaction, the rate constant for H₂O splitting is approximately 6000 and 10 times larger on Ni(110) compared to Ni(111) and Ni(100), respectively, and for OH splitting the rate constant is 200 and 3000 times bigger. The overall reaction rate for the entire water dissociation reaction decreases in the order Ni(110) > Ni(100) > Ni(111).

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References


Oxidation and Dissociation of Formyl on Ni(111), Ni(110) and Ni(100) Surfaces: A Comparative Density Functional Theory Study

Abas Mohsenzadeh1 · Kim Bolton1 · Tobias Richards1

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Abstract Formyl (CHO) is an important adsorbate and a key intermediate in industrial processes such as water gas shift (WGS), Fischer–Tropsch synthesis (FTS) and catalytic hydrocarbon combustion reactions. Density functional theory (DFT) with the PBE functional was used to calculate the adsorption, reaction and activation energies of formyl oxidation and dissociation on Ni(111), Ni(110) and Ni(100) surfaces. The results show that these energies are sensitive to the surface structure. The dissociation barrier for $\text{CHO} \rightarrow \text{CH} + \text{O}$ (FTS process) is higher than that for $\text{CHO} \rightarrow \text{CO} + \text{H}$ (catalytic combustion) on all three surfaces. This means that the dissociation to CO and H is kinetically favored. The dissociation reaction rate decreases in the order Ni(110) > Ni(111) > Ni(100) for both dissociation reactions. The formation of formate (CHO + O → HCOO), which is included in one of the pathways for the WGS reaction, has lowest activation energy on the Ni(111) surface, and the energy increases in the order Ni(111) < Ni(110) < Ni(100). However, the reaction rate at 463 K, which is a typical temperature for industrial processes that involve these reactions, is at least five orders of magnitude higher for the $\text{CHO} \rightarrow \text{CO} + \text{H}$ reaction than for the other two reactions, irrespective of the crystallographic structure of the Ni surface. This means that Ni surfaces studied here are better catalysts for this reaction. The results also show that the WGS reaction on a Ni catalyst does not primarily occur via the formate pathway.

Keywords Nickel · Formyl · Formate · Ni(111) · Ni(110) · Ni(100)

1 Introduction

A fundamental understanding of heterogeneous catalytic reactions at the microscopic level is of great importance in surface chemistry. A complete mechanistic study of the surface reactions includes the study of the elementary processes and identification of the intermediates. This is one of the reasons that adsorption of small molecules and radicals on metal surfaces has been investigated intensively using both experimental techniques and theoretical studies over the past few decades [1–9].

Oxymethylidyne (CHO) species, often referred to as formyl, is a key intermediate in many industrial processes such as water gas shift (WGS), Fischer–Tropsch synthesis (FTS) and hydrocarbon combustion reactions. The Fischer–Tropsch process is an important industrial process in which large hydrocarbons are manufactured from synthesis gas (CO/H₂ 2:1) [10]. Recent publications indicate that formyl is an important intermediate in hydrocarbon synthesis that utilizes the Fischer–Tropsch process [11, 12]. The reaction via CHO is the main reaction pathway and cleavage of the C–O bond (CHO $\rightarrow$ CH + O) is an important step in the reaction [11, 12].

Recent studies also suggest that catalytic oxidation of hydrocarbons is most likely due to the direct reaction of CH fragments with surface adsorbed oxygen. The CHO species that forms from this reaction subsequently
dissociates to yield adsorbed hydrogen and CO (CHO → CO + H) [13–15].

Goodman et al. [16] studied the kinetics of CO hydrogenation on Ni(100) using Auger Electron Spectroscopy (AES). They found that a mechanism involving hydrogenation of an active carbon species is consistent with their kinetic data, and that the turnover number for methane formation is almost the same on the Ni(111) and Ni(100) surfaces. Low energy electron diffraction (LEED) was used by Hirano and Tanaka [6, 7] to investigate the methanation reaction of CO on the Ni(100) and Ni(111) surfaces, with the aim to study why the catalytic activity of these surfaces does not appear to be sensitive to the surface structure. Their results indicate that the accumulation of overlayers of carbidic intermediates could be the reason, and they concluded that the methanation reaction on Ni(111), Ni(110) and Ni(100) surfaces involves the same chemical species that produces the carbide overlayers.

Inderwildi et al. [17] used DFT with the PW91 functional to study hydrocarbon combustion and synthesis on noble metals. They showed that formyl is an essential intermediate species in both hydrocarbon combustion and synthesis and, although different metals are used for different processes, the formation and combustion of hydrocarbons have very similar mechanisms (but in opposite directions). Using DFT with the PW91 functional, Zhu et al. [18] studied the mechanism of methane reforming on the Ni(111) surface, which includes CHO formation and decomposition. They predicted that the oxidation step determines the overall reaction rate for both the CH and C oxidation pathways. The decomposition of methanol on the Ni(100) and Ni(111) surfaces was studied by Zhou et al. [19] using DFT based on the PBE functional. They suggested that the methanol decomposition reaction mechanism may be sensitive to the surface structure, since the lowest energy reaction paths on the Ni(100) surface involves breaking both the C–H and O–H bonds, while for the Ni(111) surface only the O–H bond is broken on the lowest energy reaction path. CHO formation and decomposition were also investigated in their study. Pang et al. [20] used DFT with periodic boundary conditions and the PBE functional to investigate chemisorption of radical species, including CH₃, CH₂O and HCOO, on Ni(111), Ni(100), and Ni(110) surfaces. They found that the adsorption energies are sensitive to the surface structure and increase in the order Ni(111) < Ni(100) < Ni(110).

As mentioned above, formyl also plays a key role in the WGS reaction (CO + H₂O → CO₂ + H₂). The WGS reaction is widely used in industrial processes such as methanol synthesis. It is also one of the most important reactions in gasification, where carbonaceous materials are converted to a gaseous product that can be used to produce energy or other desirable chemicals [21–25]. The WGS reaction primarily occurs via the redox, formate, associative and carbonate mechanisms [26]. The formate (HCOO) species is central in the formate mechanism, where oxidation of CHO is one of the possible routes of HCOO formation (CHO + O → HCOO). Formate is the intermediate that has the highest concentration in the WGS reaction [27–29]. Some experimental [9, 30, 31] and computational [2, 32, 33] studies revealed that the formate might block active sites on the catalyst surface, hence lowering the catalyst activity. The studies also show that formate is a rather stable intermediate due to its high formation and decomposition barriers.

Lin et al. [2] used DFT with periodic boundary conditions and the PW91 functional to study the role of formyl in Fischer–Tropsch synthesis, combustion reactions, and the formate pathway in the WGS reaction on a series of transition metal surfaces, including the Ni(111) surface. They found that the stability of formate can be attributed to its lower formation and higher dissociation barriers in the WGS pathway. The WGS reaction and coke formation pathways on the Ni(111) and Ni(211) surfaces were studied by Catapan et al. using DFT [34] based on the PBE functional. Their results suggest that, for the WGS reaction, the carboxyl pathway is preferred on the flat Ni(111) surface, while a parallel route via formate and formyl intermediates is favored on the stepped Ni(211) surface.

In this contribution we develop a consistent picture that describes the adsorption, oxidation and dissociation of formyl on the Ni(111), Ni(110) and Ni(100) surfaces using DFT calculations. This is the first time that the same models and methods are used to investigate if the reactant, transition state or product relative energies or vibrational frequencies of formyl oxidation and dissociation are affected by the crystallographic structure of the nickel catalyst. If this is the case, then the formyl adsorption strength, dissociation and oxidation rates will depend on the type of nickel surface used as the catalyst.

2 Methods and Models

The calculations were performed using the Vienna ab initio simulation package (VASP) [35–38] implementing spin polarized DFT. The exchange–correlation was treated by the generalized gradient approximation with the Perdew, Burke and Ernzerh (GGA-PBE) functional [39]. The PBE functional was selected since it allows for comparison with previously published data for similar systems [19, 20, 34, 40]. It may be noted that this functional does not include dispersion interactions, which leads to an underestimation of the binding energy. However, it has been seen that this functional provides an accurate description of the whole series of bulk transition metals [41]. Also, since the binding
energies studied here are typically large, dispersion contributions are not as important as for intermolecular interactions and, more importantly, the relative binding energies and activation barriers on the different surfaces are not expected to be affected by the dispersion energies. It may also be noted that, although the use of different functionals may lead to differences in the absolute values, there is compelling evidence in the literature that general trends are less dependent on the type of the functional that is used [42, 43].

The projector-augmented wave method (PAW) [44, 45] was used to solve the Kohn–Sham equations. A 4 × 4 × 1 Monkhorst–Pack grid of k-points [46] was used for the numerical integration in reciprocal space. The Kohn–Sham orbitals were expanded in a plane-wave basis set using a kinetic energy cut off equal to 400 eV. Larger cut offs and orbitals were expanded in a plane-wave basis set using a numerical integration in reciprocal space. The Kohn–Sham corresponding maximum-energy image does not feel the constraint otherwise imposed on the rest of the images. A −5.0 eV Å⁻² spring force constant between images is used to relax all of the images until the force acting on each atom is <0.1 eV Å⁻¹. Calculations using a force convergence criterion of 0.01 eV Å⁻¹ changed the activation barriers by <0.2 meV. To ensure that the stationary structures were minimum energy structures (zero imaginary frequencies) or transition states (one imaginary frequency) and to calculate the vibrational partition functions and zero point vibrational energies (ZPVEs), vibrational frequency calculations were performed using ionic displacements of 0.01 Å and by diagonalizing a finite difference construction of the Hessian matrix. Only the adsorbates were allowed to move. The adsorption energies (E_ads) of the reactants and products were calculated as E_ads = E_shear−adsorbate − E_surf − E_adsorbate where E_surf is the total energy of the surface-adsorbate(s) system, E_surf is the total energy of the surface and E_adsorbate is the total energy of the isolated, geometry optimized adsorbate(s) in vacuum. The rate constants (k) were estimated from transition state theory [55] using Eq. 1.

\[ k = \left( \frac{k_B T}{h} \right) \left( \frac{q^+}{q} \right) e^{\frac{-E_a}{k_B T}} \]  

where k_B is Boltzmann’s constant, T is the absolute temperature and h is Planck’s constant. \( q \) and \( q^+ \) are the partition functions for the reactant and the transition state, respectively, and \( E_a \) is the ZPE corrected activation energy. The partition functions have been approximated assuming harmonic vibrations. Although this approximation may affect the quantitative results presented here, it is not expected to affect the trends [48, 56, 57]. It should be noted that the entropy contributions are not considered in Eq. 1. However, the effect of including entropy should not affect the relative energies since the molecules involved in the reactions are all small and have strong bonds and angles (there are no modes with small force constants that would have large entropic effects). Also, there is no significant surface reconstruction during the reactions.

The surface sites that were studied in this work are depicted schematically in Fig. 1.

3 Results and Discussion

3.1 Adsorption Energies

3.1.1 HCOO Adsorption

The HCOO adsorption strength (given in Table 1) decreases in the order Ni(110) > Ni(100) > Ni(111). As further discussed in Sect. 3.4, the surface metal atom
Coordination numbers are 9, 8 and 7 for the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The trends of adsorption energies obtained are expected since adsorbates typically bind more strongly to surfaces with low coordination numbers [20, 58, 59]. The formate is adsorbed via its two oxygen atoms on all three surfaces. Experimental studies support these results since the bidentately adsorbed formate is the species that is observed in high concentrations [2]. On the Ni(111) and Ni(110) surfaces the oxygen atoms are over the top site, A, and the other one is over a bridge site, B. As shown in Table 1, the oxygen atoms are closest to the surface on Ni(110), which is expected since this surface also has the strongest adsorption. Both C–O bonds have similar lengths on the Ni(110) and Ni(111) surfaces, but they are different on the Ni(100) surface where the distance between the carbon and oxygen atom on the bridge site is about 0.35 Å longer than the other C–O bond. Similar to the bond lengths, both O–C–H angles are the same on the Ni(111) and Ni(110) surfaces, but on the Ni(100) surface one angle is about 2.2° larger than the other. Similar C–O bond lengths and O–C–H angles on the Ni(111) and Ni(110) surfaces are expected since both oxygen atoms adsorbs on top, A, sites. In contrast, these atoms adsorb on different sites (one on the A site and the other one on B site) on the Ni(100) surface.

The calculated energies of adsorption are comparable with most of the previous results (references given in the Table 1). Pang et al. [20] (using GGA-PBE on a three layered 2 × 2 unit cell and three layer slab) reported an adsorption energy of −0.86, −1.60 and −1.07 eV for the Ni(111), Ni(110) and Ni(100) surfaces, respectively. The discrepancy between those results and the data presented here is due to the different methods used for calculating the adsorption energies. They defined the binding energy of formate with respect to the gas phase CO2 and H2. Using the same method we obtain adsorption energies of −0.46, −1.06 and −0.65 eV for the Ni(111), Ni(110) and Ni(100) surfaces, respectively. In this work, the energies calculated for isolated H2 and CO2 are −6.49 and −22.67 eV, respectively. The trends observed for adsorption, oxidation and dissociation of all of the species studied here, including HCOO, are discussed further in Sect. 3.4.

The experimentally observed vibrational frequencies for HCOO on Ni(110) reported by Madix et al. [60] are in good agreement with the calculated vibrational frequencies. They observed bidentately adsorbed HCOO and reported 2950 cm−1 as the C–H bond stretching frequency (compared to 2961 cm−1 calculated here), 1670 cm−1 as the O–C–H bending frequency, and 1150 cm−1 as the C–O stretching frequency.

### Table 1 Adsorption energies (eV), structural parameters (Å and °) for adsorbed HCOO

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>E_{ads}</th>
<th>d_{surf-O}^b</th>
<th>d_{C-O}^b</th>
<th>θ_{O-C-H}^b</th>
<th>Previous results for E_{ads}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)</td>
<td>O1: A</td>
<td>−2.69</td>
<td>1.961</td>
<td>1.272</td>
<td>O1–C–H: 116.4</td>
<td>−3.14e, −0.86e, −3.02e</td>
</tr>
<tr>
<td></td>
<td>O2: A</td>
<td></td>
<td>1.963(B)</td>
<td>1.271(B)</td>
<td>O2–C–H: 116.4(B)</td>
<td></td>
</tr>
<tr>
<td>Ni(110)</td>
<td>O1: A</td>
<td>−3.29</td>
<td>1.921</td>
<td>1.272</td>
<td>O1–C–H: 115.1</td>
<td>−1.60d</td>
</tr>
<tr>
<td></td>
<td>O2: A</td>
<td></td>
<td>1.921(B)</td>
<td>1.272(B)</td>
<td>O2–C–H: 115.1(B)</td>
<td></td>
</tr>
<tr>
<td>Ni(100)</td>
<td>O1: B</td>
<td>−2.88</td>
<td>2.028</td>
<td>1.294</td>
<td>O1–C–H: 115.8</td>
<td>−1.07d</td>
</tr>
<tr>
<td></td>
<td>O2: A</td>
<td></td>
<td>1.963(B)</td>
<td>1.259(B)</td>
<td>O2–C–H: 118.0(B)</td>
<td></td>
</tr>
</tbody>
</table>

The adsorption energies are ZPVE-corrected values

- **a** Shortest distance between the oxygen atom of the adsorbate and any metal atom on the surface
- **b** (B) refers to the bond which is broken during the reaction
- **c** Ref. [2] (GGA-PW91 calculations using a 4 × 4 unit cell and five layer slab
- **d** Ref. [20] (GGA-PBE calculations using a 3 × 2 unit cell and three layer slab
- **e** Ref. [34] (GGA-PBE calculations using a 2 × 2 unit cell and four layer slab

---

**Fig. 1** Different adsorption sites on the Ni(111), Ni(110) and Ni(100) surfaces. A is a top site; B is a bridge site; C is an hcp site; C’ is a fcc site; D is a rectangular fourfold hollow site; D’ is a square fourfold hollow site; E is a long bridge site; F is a short bridge site; G is a pseudo threefold hollow site.
the frequency of the asymmetric vibration of the
O–C–O bond (compared to 1504 cm$^{-1}$ calculated here),
1370 cm$^{-1}$ for the O–C–O symmetric vibration (compared
to 1296 cm$^{-1}$ calculated here), and 780 cm$^{-1}$ as the fre-
quency for the O–C–O angle (compared to 710 cm$^{-1}$ cal-
culated here).

3.1.2 CHO Adsorption

As shown in Table 2, the strongest adsorption for CHO is
obtained for the Ni(100) surface. It is $-2.76$ eV compared
to $-2.42$ eV for the Ni(110) surface and $-2.19$ eV for the
Ni(111) surface. This is in contrast to the trend that
molecules bind most strongly to surface with the lowest
coordination number which, as described above, is the
Ni(111) surface. This could be due to the orientation of the
CHO molecule on the Ni(100) surface, since the C–O bond
is almost parallel to the surface, while the carbon atom
points towards the surface on the other two surfaces. The
calculated adsorption energies are in agreement with pre-
vious experimental and theoretical results (references given
in the Table 2). For example Zhou et al. [19] (using GGA-
PBE on a three layered 3 × 2 unit cell) reported a higher
bonding energy for the Ni(100) surface compared to the
Ni(111) surface, i.e., $-3.15$ and $-2.41$ eV, respectively.
Blaylock et al. [61] reported experimental adsorption heats
of $-1.99$ and $-2.51$ eV on the Ni(111) and Ni(100) sur-
faces, which are comparable to the values reported in this
work and also follow the same trends.

The surface-carbon distance is shortest on the Ni(110)
surface. The surface-oxygen distance is the same for the
Ni(111) and Ni(110) surfaces, and is a bit larger than for the
Ni(100) surface.

The C–H bond length on the Ni(110) surface is larger by
about 0.06 and 0.05 Å compared to the Ni(111) and

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>$E_{ads}$</th>
<th>$d_{surf-C}$</th>
<th>$d_{surf-O}$</th>
<th>$d_{C-H}$</th>
<th>$d_{C-O}$</th>
<th>$\theta_{O-C-H}$</th>
<th>$\alpha$</th>
<th>Previous results for $E_{ads}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)</td>
<td>C: B</td>
<td>$-2.19$</td>
<td>1.960</td>
<td>1.969</td>
<td>1.110</td>
<td>1.289</td>
<td>117.0</td>
<td>16.1</td>
<td>$-2.63^c$, $-2.41^d$, $-2.49^e$, $-2.26^f$</td>
</tr>
<tr>
<td></td>
<td>O: A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(110)</td>
<td>C: F</td>
<td>$-2.42$</td>
<td>1.807</td>
<td>1.969</td>
<td>1.116</td>
<td>1.257</td>
<td>117.9</td>
<td>10.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O: A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(100)</td>
<td>C: B</td>
<td>$-2.76$</td>
<td>1.916</td>
<td>1.960</td>
<td>1.111</td>
<td>1.353</td>
<td>112.5</td>
<td>5.6</td>
<td>$-3.15^f$</td>
</tr>
<tr>
<td></td>
<td>O: B</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The adsorption energies are ZPVE-corrected values

a Shortest distance between the oxygen and carbon atoms of the adsorbate and any metal atom on the surface
b The angle between the C–O bond and the surface plane
c Ref. [2] (GGA-PW91 calculations using a 4 × 4 unit cell and five layer slab)
d Ref. [19] (GGA-PBE calculations using a 3 × 2 unit cell and three layer slab)
e Ref. [34] (GGA-PBE calculations using a 2 × 2 unit cell and four layer slab)
f Ref. [18] (GGA-PW91 calculations using a 3 × 3 unit cell and four layer slab)
that was seen for CHO adsorption in the absence of oxygen. Both formyl and oxygen are closest to the surface on the Ni(110) surface. The distance between the formyl and surface is not changed significantly due to the presence of the O atom. Due to the presence of the co-adsorbed oxygen atom, the C–O bond lengths are shorter compared to isolated formyl adsorbed on the surface and the formyl O–C–H angle is increased. No previous results for the co-adsorption of CHO and O have been found.

The formyl dissociation in FTS yields CH and O [17]. The co-adsorption energies for CHO dissociation products are $-10.81$, $-11.89$, and $-12.28$ eV on the Ni(111), Ni(110) and Ni(100) surfaces, respectively (given in Table 4). The co-adsorption sites are the same as those found for the isolated adsorbates, except for the oxygen on the Ni(110) surface which is shifted from the E site to the G site. This is probably due to interaction with co-adsorbed CH as this was also observed for co-adsorbed CHO and O. The shortest surface-adsorbate distance was obtained on the Ni(111) surface for both CH and O. The C–H bond is almost the same on the Ni(100) and Ni(110) surfaces and is a bit longer than that on the Ni(111) surface. The co-adsorption energy on the Ni(111) surface is comparable to what is obtained by Wang et al. [40] (using GGA-PBE on a three layered $2 \times 2$ unit cell), i.e., $-10.61$ eV. No data was found for the other surfaces.

The CHO dissociation in hydrocarbon combustion yields CO and H [17]. The co-adsorption energies (given in Table 5) of CO and H are $-4.54$, $-4.51$, and $-4.61$ eV on the Ni(111), Ni(110) and Ni(100) surfaces, respectively. In all cases the co-adsorption sites are the same as those found for the isolated adsorbates. Both CO and H are closest to the Ni(110) compared to the other surfaces. The shortest C–O bond is also found for the Ni(110) surface. The co-adsorption energy on the Ni(111) surface is comparable to what is obtained by Wang et al. [40] (using GGA-PBE on a three layered $2 \times 2$ unit cell), i.e., $-4.58$ eV. No data was found for the other surfaces.

### 3.3 Transition States and Reaction Energies

#### 3.3.1 HCOO Formation

The transition states and reaction rate constants for formate formation are presented in Table 6. The rate constants are calculated at 463 K, which is typical for low-temperature WGS processes [62]. The activation barriers are $0.67$ eV, $0.99$ eV and $1.47$ eV for the Ni(111), Ni(110) and Ni(100)
surfaces, respectively. The activation energy obtained for the Ni(111) surface is slightly lower than those reported by Lin et al. [2] (using GGA-PW91 on a five layered 4 x 4 unit cell) (0.94) eV and Catapan et al. [34] (using GGA-PBE on a four layered 2 x 2 unit cell) (0.74 eV). No results for the Ni(110) and Ni(100) surfaces are available. The activation energy is lowest on the Ni(111) surface. The reaction is exothermic on all surfaces with a reaction energy of – 0.85 eV, – 0.7 and – 0.10 eV on the Ni(111), Ni(110) and Ni(100) surfaces, respectively.

As is discussed in Sect. 3.4., the calculated d-band centres are at – 1.75, – 1.98 and – 2.08 eV for the Ni(110), Ni(100) and Ni(111) surfaces, respectively [63]. One may consider the Ni(110) surface as the most reactive since, in general, the closer the d-band center to the Fermi level, the more reactive the surface [3, 64]. However the lowest barrier was obtained on the Ni(111).

The Brønsted–Evans–Polanyi (BEP) principle states that the activation energy for a given reaction should be linearly proportional to the reaction energy [65, 66]. The energetics obtained for this reaction support the BEP principle with R² value of 0.94 (E_a = 0.96 E_\text{react} – 1.56, R² = 0.94). It should be noted that only three nickel facets have been studied in this work and more facets are needed to improve the statistical relevance of the results.

Previous experimental studies by Benziger et al. [67, 68] indicate that the surface structure plays a key role in the kinetics of the formic acid decomposition reaction, where the formate species is involved, on the Ni(111), Ni (110) and Ni(100) surfaces. The energetics obtained by the

### Table 5: Co-adsorption energies (eV) and structural parameters (Å and °) of for CO and H

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>E_ads</th>
<th>d_{surf-C}^a</th>
<th>d_{surf-H}</th>
<th>d_{C-O}</th>
<th>Previous results for E_ads</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111) C: C</td>
<td>-4.54</td>
<td>1.947</td>
<td>1.694</td>
<td>1.191</td>
<td>-4.58b</td>
<td></td>
</tr>
<tr>
<td>H: C'</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(111) C: F</td>
<td>-4.51</td>
<td>1.874</td>
<td>1.691</td>
<td>1.181</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H: G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(110) C: D'</td>
<td>-4.61</td>
<td>2.037</td>
<td>1.833</td>
<td>1.213</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H: D'</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Shortest distance between any metal atom on the surface and the carbon atom of the CO and the co-adsorbed hydrogen atom.

(b) Ref. [40] (GGA-PBE calculations using a 2 x 2 unit cell and three layer slab).

### Table 6: CHO + O → HCOO activation energies (eV), reaction rate constant at 463 K (s⁻¹), reaction energy (eV), length of the forming C–O bond at the transition state (Å) and its imaginary frequency (cm⁻¹) and O–C–H angle (°)

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>E_a</th>
<th>ΔE</th>
<th>d_{C-O}^a</th>
<th>\theta_{O-C-H}</th>
<th>Imaginary frequency</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111) C: B</td>
<td>0.67</td>
<td>-0.85</td>
<td>1.256</td>
<td>112.4</td>
<td>427</td>
<td>6.66 \times 10^3</td>
<td></td>
</tr>
<tr>
<td>O_{CHO}: B</td>
<td>1.860(B)</td>
<td>95.0(B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Previous results</td>
<td>0.94b, 0.74c</td>
<td>-0.39c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(110) C: G</td>
<td>0.99</td>
<td>-0.72</td>
<td>1.275</td>
<td>112.1</td>
<td>431</td>
<td>5.79 \times 10^3</td>
<td></td>
</tr>
<tr>
<td>O_{CHO}: G</td>
<td>1.828(B)</td>
<td>95.0(B)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Previous results</td>
<td>0.74a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(100) C: D</td>
<td>1.47</td>
<td>-0.10</td>
<td>1.312</td>
<td>117.9</td>
<td>501</td>
<td>1.62 \times 10^-3</td>
<td></td>
</tr>
<tr>
<td>O_{CHO}: D</td>
<td>1.823(B)</td>
<td>96.4</td>
<td></td>
<td></td>
<td></td>
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<td>Previous results</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) \( (B) \) refers to the bond which is formed during the reaction.

(b) Ref. [2] (GGA-PW91 calculations using a 4 x 4 unit cell and five layer slab).

(c) Ref. [34] (GGA-PBE calculations using a 2 x 2 unit cell and four layer slab).
present DFT calculations are consistent with these observations.

The length of the forming C–O bond in the transition state structure on the Ni(111) surface is about 0.32 and 0.37 Å longer compared to the Ni(110) and Ni(100) surfaces, respectively, and its imaginary vibrational frequency is the lowest. On all surfaces, the forming O–C–H bond angle in the transition state structures are nearly the same and smaller compared to the product, i.e., HCOO (see Table 2). The lower activation energy on the Ni(111) surface, together with differences in the vibrational frequencies, lead to the large rate constant observed on this surface.

The geometries of the reactants, transition states and products that are detailed in Table 6, are shown in Fig. 2.

### 3.3.2 CHO Dissociation to CH and O

Table 7 shows the details of the transition states of the formyl dissociation to CH and O. The calculated activation energies are 1.16, 0.89 and 1.86 eV for the Ni(111), Ni(110) and Ni(100) surfaces, respectively. The trends of the activation barriers are consistent with the distance of d-band center from the Fermi level (discussed above). However, the fit to the BEP principle with an $R^2$ value of 0.10 ($E_a = -0.29 E_{react} + 0.11$, $R^2 = 0.10$) is not as good as the CHO oxidation reaction.

The reaction energies are 0.30 eV on the Ni(111) surface, $-0.54$ eV on the Ni(110) surface and $-0.59$ eV on the Ni(100) surface. Hence, the reaction is exothermic on the Ni(110) and Ni(100) surfaces while it is endothermic on Ni(111). This is probably due to much weaker adsorption of the CH and O products on the Ni(111) surface. The activation energy obtained for the Ni(111) surface is similar to that reported by Zhu et al. [18] (using GGA-PW91 on a four layered $3 \times 3$ unit cell), i.e., 1.08 eV and is lower than that reported by Catapan et al. [34] (using GGA-PBE on a four layered $2 \times 2$ unit cell), i.e., 1.28 eV. Lin et al. [2] (using GGA-PW91 on a five layered $4 \times 4$ unit cell) reported a barrier of 0.79 eV and an exothermic reaction on the Ni(111) surface. This exothermicity could be due to the fact that they used a larger $4 \times 4$ supercell, since the adsorption energy of the CH and O products may be reduced (due to increased surface area) relative to the CHO reactant [69]. The length of the breaking C–O bond of the transition state structure on the Ni(110) surface is shorter compared to the Ni(111) and Ni(100) surfaces.

The reaction rate constants are significantly influenced by the structure of the surface. At 463 K the rate constant is very small for the Ni(100) surface due to the high energy barrier obtained for this surface. The geometries of the reactants, transition states and products are shown in Fig. 3.

### 3.3.3 CHO Dissociation to CO and H

Details of the transition states for the formyl dissociation to CO and H are given in Table 8. The activation energies are 0.15 eV for the Ni(111) surface, 0.16 eV for the Ni(110) surface and 0.48 eV for the Ni(100) surface. The trends of the activation barriers are on contradiction to what is
expected from the distance of d-band center from the Fermi level, although the energetics obtained for these reactions support the BEP principle with an R² value of 0.78 (E_a = 1.17E_{\text{react}} - 1.44, R² = 0.78).

The reaction over all three surfaces is exothermic with reaction energies of -1.38, -1.13 and -0.88 eV for the Ni(111), Ni(110) and Ni(100) surfaces, respectively. The results are comparable to previous theoretical and experimental studies. For example Zhu et al. [18] (using GGA-PW91 on a four layered 3 × 3 unit cell) reported an energy barrier of 0.18 eV and a reaction energy of -1.34 eV on the Ni(111) surface. Goodman et al. [16] found a CO hydrogenation barrier of 1.07 eV on the Ni(100) surface using Auger Electron Spectroscopy (AES) compared to 1.29 eV obtained in this work (activation energy for backward CHO → CO + H reaction). Kao et al. [70] used a combined ultrahigh-vacuum surface analysis-high-pressure cell system to measure a barrier equal to 1.16 eV for CO hydrogenation on the Ni(111) surface, which is comparable to the activation energy reported here i.e. 1.53 eV. The trends reported in these experimental studies are similar to what is found in the present study i.e. the

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**Table 7** CHO → CH + O activation energies (eV), reaction rate constant at 463 K (s⁻¹), reaction energy (eV), length of the breaking O–C–H angle (°)

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>E_a</th>
<th>ΔE</th>
<th>d_C-O</th>
<th>θ_O-C-H</th>
<th>Imaginary frequency</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)</td>
<td>C: B</td>
<td>1.16</td>
<td>0.30</td>
<td>1.820</td>
<td>94.7</td>
<td>525</td>
<td>6.65 × 10⁻¹</td>
</tr>
<tr>
<td></td>
<td>O: B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Previous results</td>
<td></td>
<td>0.79⁴, 1.28⁵, 1.08⁶</td>
<td>-0.46⁷</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(110)</td>
<td>C: E</td>
<td>0.89</td>
<td>-0.54</td>
<td>1.848</td>
<td>89.6</td>
<td>443</td>
<td>3.49 × 10²</td>
</tr>
<tr>
<td></td>
<td>O: G</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Previous results</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(100)</td>
<td>C: B</td>
<td>1.86</td>
<td>-0.59</td>
<td>1.958</td>
<td>92.7</td>
<td>450</td>
<td>5.09 × 10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>O: B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Previous results</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The activation and reaction energies are ZPVE-corrected values

⁴ Ref. [2] (GGA-PW91 calculations using a 4 × 4 unit cell and five layer slab)
⁵ Ref. [34] (GGA-PBE calculations using a 2 × 2 unit cell and four layer slab)
⁶ Ref. [18] (GGA-PW91 calculations using a 3 × 3 unit cell and four layer slab)

---

**Fig. 3** Reactant, transition state and product structures for the CHO → CH + O reaction
The breaking C–H bond of the transition state structure on the Ni(100) surface is about 0.15 Å longer compared to the other surfaces. At 463 K, the rate constants are similar for the Ni(111) and Ni(110) surfaces and approximately 500 times bigger than that obtained for the Ni(100) surface. Figure 4 shows the geometries of the reactants, transition states and products.

### 3.4 Comparison of the Adsorption Energies and Reaction Barriers Obtained on the Different Ni Surfaces

Adsorbates typically bind more strongly to high symmetry sites than to low symmetry sites, and to atoms with low coordination numbers rather than high coordination numbers [20, 58, 59]. The surface metal atoms coordination numbers are 9, 8 and 7 for the Ni(111), Ni(100) and Ni(110) surfaces, respectively. Hence, one may expect strongest adsorption on the Ni(110) surface. The projected density of states (PDOS) of the metallic Ni d-band can also describe the physical origin of the difference in catalytic activity for the different surfaces [20, 50, 64]. We have seen previously that all of the adsorbates are more negatively charged than when they are in vacuum [52]. This extra electron density is assumed to come from the frontier d orbitals of the metal surface. The intensities of the occupied orbitals at the Fermi level are 2.0, 2.2 and 2.7 states/eV for the Ni(111), Ni(100) and Ni(110) surfaces, respectively [63]. Thus the Ni(110) surface can donate a higher electron density to the adsorbate. Hence, both the differences in electron density and coordination number can explain why the adsorption energies of HCOO decrease in the order Ni(110) > Ni(100) > Ni(111). However, for the CHO adsorbate and the co-adsorbed species the binding energies are largest on the Ni(100) surface. The reason for the higher binding energy for CHO on the Ni(100) surface could be due to the orientation of formyl molecule on the surface. On the Ni(100) surface, the C–O bond is almost parallel to the surface plane, whereas the carbon atom is pointing down on the other surfaces. The angle between the C–O bond and the surface plane is 5.6°, 10.7° and 16.1° on the Ni(100), Ni(110) and Ni(111) surfaces, respectively (see Table 2). Similar trends have been found by Zhou et al. [19] (using GGA-PBE on a three layered 3×2 unit cell), who obtained adsorption energies of −2.41 eV and −3.15 eV on Ni(111) and Ni(100) surfaces, respectively. Similarly to CHO, co-adsorption of CHO+O and CH+O is strongest on the Ni(100) surface. Also, similarly to CHO, co-adsorption of CHO+O and CH+O is stronger on the Ni(110) surface than on the Ni(111) surface. In contrast, CO+H co-adsorption is stronger on the Ni(111) surface than on the Ni(110) surface.

The reaction profiles for the oxidation and dissociation of formyl are compared in Fig. 5. It is evident that the activation energies for CHO dissociation to CO and H are smaller on all surfaces compared to the oxidation reaction and the dissociation of CHO to CH and O. Hence, adsorbed CHO species are far more likely to dissociate to CO and H than to CH and O or to react with a co-adsorbed oxygen atom. It can be noted that no consistent correlations could be found between the transition state geometries and the

### Table 8  
CHO → CO + H activation energies (eV), reaction rate constant at 463 K (s⁻¹), reaction energy (eV), length of the breaking C–H bond at the transition state (Å) and its imaginary frequency (cm⁻¹) and O–C–H angle (°)

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>E_a</th>
<th>ΔE</th>
<th>d_C–H</th>
<th>θ</th>
<th>Imaginary frequency</th>
<th>k</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)</td>
<td>C: C</td>
<td>0.15</td>
<td>−1.38</td>
<td>1.155</td>
<td>118.6</td>
<td>290</td>
<td>1.51 × 10¹¹</td>
</tr>
<tr>
<td>Ni(110)</td>
<td>C: B</td>
<td>0.16</td>
<td>−1.13</td>
<td>1.159</td>
<td>122.5</td>
<td>313</td>
<td>2.20 × 10¹¹</td>
</tr>
<tr>
<td>Ni(100)</td>
<td>C: D</td>
<td>0.48</td>
<td>−0.88</td>
<td>1.306</td>
<td>114.8</td>
<td>179</td>
<td>3.85 × 10⁸</td>
</tr>
<tr>
<td>Previous results</td>
<td>O: A</td>
<td>0.29⁹, 0.27⁸, 0.18⁸, 0.20¹⁰</td>
<td>−1.18⁹, −1.18⁸, −1.34¹⁰</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The activation and reaction energies are ZPVE-corrected values
  ᵈ Ref. [40] (GGA-PBE calculations using a 2 × 2 unit cell and three layer slab)
  ᵇ Ref. [2] (GGA-PW91 calculations using a 4 × 4 unit cell and five layer slab)
  ᵆ Ref. [19] (GGA-PBE calculations using a 3 × 2 unit cell and three layer slab)
  ᵉ Ref. [18] (GGA-PW91 calculations using a 3 × 3 unit cell and four layer slab)
surface atom charge densities or surface d-band centres (which describes the distribution of surface electronic energy levels and demonstrates the ability to eject an electron from the d-band of the metal to the adsorbate [3, 64]). However the energetics obtained for formyl oxidation and for dissociation to CO + H support the BEP principle with R^2 value of 0.94 and 0.78. The R^2 value for CHO dissociation to CH and O is 0.10.

4 Conclusions

Formyl is an important adsorbate and a key intermediate in many industrial processes. A fundamental understanding of aspects that affect the reactivity of this intermediate and its dissociation and oxidation reactions, such as the catalytic surface structure, is expected to assist in the development of more efficient catalysts.
The effect of three common nickel surface structures on the adsorption and reaction energies of formyl oxidation and dissociation has been studied by DFT calculations using the same models and methods for all surfaces. The results show that the adsorption energies and reaction barriers are sensitive to the surface structure. For the dissociation of CHO, the barrier for CHO → CH + O (FTS process) is higher than that for CHO → CO + H (catalytic combustion) on all three surfaces. The dissociation reaction rate constant decreases in the order Ni(110) > Ni(111) > Ni(100). For the formation of formate (CHO + O → HCOO), the lowest activation barrier is on the Ni(111) surface and increases in the order Ni(111) < Ni(110) < Ni(100). On Ni(111), the barrier for CHO → CH + O and CHO + O → HCOO is seven and four times higher, respectively, compared to CHO → CO + H. Consequently the reaction rate constant for CHO → CO + H, at 463 K, is 3 × 10^{12} and 3 × 10^{6} times larger than those for formate formation and formyli dissociation to CH and O.

Irrespective of the crystallographic structure of the Ni surfaces, the barrier for dissociation of CHO to CO and H is lower compared to the other two reactions. This means that formyl prefers to dissociate to CO and H instead of reacting with co-adsorbed oxygen atoms or dissociating to CH and O. This means that Ni performs better for this reaction (catalytic combustion) compared to the FTS process. However more investigations of different possible intermediate species and reactions are needed to clarify the nature of the interaction between catalyst surface and reaction intermediates and to draw a more realistic picture of the mechanism of these reactions. The results also indicate that the WGS reaction with a Ni catalyst does not, to a large extent, occur via the formate pathway.

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References
Paper IV
A density functional theory study of hydrocarbon combustion and synthesis on Ni surfaces

Abas Mohsenzadeh · Tobias Richards · Kim Bolton

Abstract Combustion and synthesis of hydrocarbons may occur directly (CH → C + H and CO → C + O) or via a formyl (CHO) intermediate. Density functional theory (DFT) calculations were performed to calculate the activation and reaction energies of these reactions on Ni(111), Ni(110), and Ni(100) surfaces. The results show that the energies are sensitive to the surface structure. The dissociation barrier for methylidyne (CH → C + H: catalytic hydrocarbon combustion) is lower than that for its oxidation reaction (CH + O → CHO) on the Ni(110) and Ni(100) surfaces. However the oxidation barrier is lower than that for dissociation on the Ni(111) surface. The dissociation barrier for methylidyne dissociation decreases in the order Ni(111) > Ni(100) > Ni(110). The barrier of formyl dissociation to CO and H is almost the same on the Ni(111) and Ni(110) surfaces and is lower compared to the Ni(100) surface. The energy barrier for carbon monoxide dissociation (CO → C + O: catalytic hydrocarbon synthesis) is higher than that of its hydrogenation reaction (CO + H → CHO) on all three surfaces. This means that the hydrogenation to CHO is favored on these nickel surfaces. The energy barrier for both reactions decreases in the order Ni(111) > Ni(100) > Ni(110). The barrier for formyl dissociation to CH + O decreases in the order Ni(100) > Ni(111) > Ni(110). Based on these DFT calculations, the Ni(110) surface shows a better catalytic activity for hydrocarbon combustion compared to the other surfaces, and Ni is a better catalyst for the combustion reaction than for hydrocarbon synthesis, where the reaction rate constants are small. The reactions studied here support the BEP principles with R² values equal to 0.85 for C-H bond breaking/forming and 0.72 for C-O bond breaking/forming reactions.

Keywords DFT · Hydrocarbon combustion · Hydrocarbon synthesis · Nickel

Introduction

The environmental consequences caused by fossil fuel combustion, such as production of pollutants and greenhouse gases, increases the importance of sustainable energy sources. Gasification is one of the most important and effective methods for sustainable energy generation. Generally, gasification means the conversion of carbonaceous material to a gaseous product, i.e., carbon monoxide and hydrogen (synthesis gas which is often referred to as syngas) with an employable heating value [1]. This gaseous product can further be converted into other hydrocarbons and liquid fuels that are combusted to H₂O and CO₂.

Catalytic combustion of hydrocarbons is an important technology, and has been developed for efficient energy production with minimum pollutant formation. It is done at lower temperatures compared to conventional flame combustion. The catalyst has played a decisive role in the improvement of this process [2–4]. Recent studies revealed that hydrocarbon oxidation is not a simple dissociation of the hydrocarbon
into hydrogen and carbon followed by oxidation reactions as assumed in previous studies [5, 6]. Instead, the direct reaction between CH fragments and oxygen can be the most important pathway. In this mechanism, an oxymethylidyne (CHO, formyl) intermediate is formed and subsequently dissociates to hydrogen and carbon monoxide [7, 8].

Since the early developmental work by Fischer and Tropsch and their co-workers [9], the synthesis of hydrocarbons from syngas is probably the most important source of chemicals and fuels from non-petroleum based sources. Fischer-Tropsch synthesis (FTS) is a complex catalytic process in which the synthesis gas is converted into various hydrocarbons and water over transition metals [10, 11]. The produced hydrocarbons can be utilized as feedstock in the chemical industry or as fuel. FTS has been investigated experimentally [12–14] and theoretically [8, 15, 16]. For the synthesis of hydrocarbons, a conclusion that was drawn from earlier studies was that both CO and H₂ are adsorbed on the catalyst surface and subsequently dissociate. Then both the C and O species are hydrogenated to CH₂ and H₂O [17]. However, recent investigations suggest that the reaction via CHO species is the main reaction pathway, similar to catalytic hydrocarbon combustion [18–21].

Inderwildi et al. [18] used DFT calculations and microkinetic simulations to study the FTS mechanism on a cobalt surface, and demonstrated that the main reaction pathway is the hydrogenation of CO (forming CHO) and subsequent cleavage of the C-O bond which yields co-adsorbed CH and O. They also investigated catalytic combustion and synthesis on noble metals [8], and found that the combustion and formation of hydrocarbons follow very similar routes but in opposite directions, and that CHO is an essential intermediate in both processes.

Zhu et al. [22] performed DFT calculations to investigate the methane reforming mechanism on the Ni(111) surface, which includes CHO formation and decomposition. They suggested that the oxidation step determines the overall reaction rate for both CH and C oxidation pathways. DFT calculations were used to study methanol decomposition on the Ni(111) and Ni(100) surfaces by Zhou et al. [23]. CHO formation and decomposition were also investigated in their study. They concluded that the methanol decomposition reaction mechanism may be sensitive to the surface structure. Wang et al. [24] investigated the reaction pathways of CO₂ reforming of CH₄ on the Ni(111) surface using DFT calculations. They found that CH oxygenation into CHO is more favored than its dissociation to C and H.

Goodman et al. [25] used Auger electron spectroscopy (AES) to investigate the kinetics of CO hydrogenation on the Ni(100) surface. Their results showed that a mechanism involving hydrogenation of an active carbon species was consistent with their kinetic data, and that the turnover number for methane formation is similar on the Ni(111) and Ni(100) surfaces. Hirano and Tanaka et al. [26, 27] used low energy electron diffraction (LEED) to study the methanation reaction of CO on Ni(111), Ni(110), and Ni(100) surfaces, and to explain why the catalytic activity of these surfaces does not appear to be sensitive to the surface structure. They found that the accumulation of overlayers of carbide intermediates could be the reason. They concluded that the methanation reaction is catalyzed by the same compound that produces the carbide overlayers.

In contrast to methanation of CO on Ni surfaces, many studies indicate that the catalytic properties and reaction energies are affected by surface orientation, steps and defects [28–30]. Nickel particles grown on oxide or graphite substrates have polyhedral shapes exhibiting (111), (110), and (100) facets [31]. These facets have been investigated both theoretically and experimentally. As discussed above, investigations, e.g., of methanol decomposition, have been performed on the Ni(111) and Ni(100) surfaces, showing that they are stable under experimental conditions. The Ni(110) surface is also stable under experimental conditions. For example, Madix et al. [32] used high resolution electron energy loss vibrational spectroscopy to study the intermediate formed in the dehydration reaction for formic acid on Ni(110). They suggested that the lateral interactions between CO and HCOO cause the autocatalytic decomposition of the formate.

The present contribution provides a comparative DFT study of the combustion and the synthesis of hydrocarbons on the Ni(111), Ni(110), and Ni(100) surfaces. To the best of our knowledge this is the first time that the same methods and models are used for all surfaces and reactions to investigate how the reactant, transition state or product relative energies or vibrational frequencies are affected by the crystallographic structure of the nickel catalyst. These results are analyzed to identify which of the hydrocarbon combustion and synthesis reactions are kinetically favored on each of the surfaces, and whether these reactions follow the Brønsted-Evans-Polanyi (BEP) principles.

Methods and models

The calculations were performed using the Vienna ab initio simulation package (VASP) [33–36] implementing spin polarized DFT. The generalized gradient approximation with the Perdew, Burke, and Ernzerh of (GGA-PBE) formulation was used for the exchange-correlation functional [37]. The Kohn-Sham equations were solved using the projector-augmented wave method (PAW) [38, 39] with a 4×4×1 Monkhorst-Pack grid of k-points [40] for the numerical integration in reciprocal space. The Kohn-Sham orbitals were expanded in a plane-wave basis set using a kinetic energy cut off of 400 eV. Larger cut offs and finer k-meshes were also examined and yielded the same trends reported below. The conjugate-gradient (CG)
method was used for geometry optimization, and the minimum energy structure was identified when the change in the total energy and the forces acting on each ion became smaller than $10^{-5}$ eV and $10^{-3}$ eVÅ$^{-1}$, respectively.

A four-layer slab with a 2×2 unit cell was used to model the Ni surfaces. To provide a representative model of the semi-infinite bulk crystal, the two bottom layers of the slab were fixed and the two upper layers were free to relax. This slab size corresponds to a 1/4 and 1/2 monolayer coverage when there are one or two adsorbates, respectively, on the surface. This unit cell size yields converged results in a computationally feasible time and has been commonly used in investigations of similar systems [41–43]. Earlier studies have also shown that similar trends are obtained at lower surface coverages [44].

Transition states were found using the climbing image-nudged elastic band method [45, 46], where six images were placed between the reactant and product geometries. A $-5.0$ eVÅ$^{-2}$ spring force constant between images was used to relax the images until the maximum force acting on each ion was less than $0.1$ eVÅ$^{-1}$. Calculations using a higher force convergence criterion of $0.01$ eVÅ$^{-1}$ changed the activation barrier by less than $0.2$ meV. To confirm that the stationary structures were minimum energy (zero imaginary frequencies) or transition states (one imaginary frequency) and to calculate the vibrational partition functions and zero point vibrational energies (ZPVEs), vibrational frequency calculations were performed using ionic displacements of $0.01$ Å. Only the adsorbates were allowed to move, and the frequencies were obtained by diagonalizing the finite difference Hessian matrix. This method has been successfully used in previous studies [47–49].

The adsorption energies ($E_{\text{ads}}$) of the reactants and products were calculated as $E_{\text{ads}} = E_{\text{surf+adsorbate}} - E_{\text{surf}} - E_{\text{adsorbate}}$ where $E_{\text{surf+adsorbate}}$ is the total energy of the surface-adsorbate(s) system, $E_{\text{surf}}$ is the total energy of the surface and $E_{\text{adsorbate}}$ is the total energy of the isolated, geometry optimized adsorbate(s) in vacuum. The rate constants ($k$) were estimated from transition state theory [50] using Eq. 1:

$$k = \left( \frac{k_B T}{\hbar} \right) \left( \frac{q^+}{q} \right) e^{-\frac{E_a}{k_B T}},$$

where $k_B$ is Boltzmann’s constant, $T$ is the absolute temperature, and $\hbar$ is Planck’s constant. $q$ and $q^+$ are the partition functions for the reactant and the transition state, respectively, and $E_a$ is the ZPVE corrected activation energy. The partition functions were calculated using harmonic vibrations. Although this approximation may affect the quantitative results presented here, it is not expected to affect the trends [29, 47, 51].

The different surface sites that are present on the Ni(111), Ni(110), and Ni(100) surfaces and that were investigated are shown in Fig. 1.

The first principles data were used to model the kinetics of the hydrocarbon synthesis reaction via the direct dissociation route ($\text{CO} \rightarrow \text{C} + \text{O}$ followed by $\text{C} + \text{H} \rightarrow \text{CH}$) and the formyl route ($\text{CO} + \text{H} \rightarrow \text{CHO}$ followed by $\text{CHO} \rightarrow \text{CH} + \text{O}$). The ODE23s solver in the MATLAB R2013a simulation package [52] was employed to solve the ordinary differential equations for the mechanisms discussed below.

**Results and discussion**

Geometry optimizations were performed for all adsorption sites shown in Fig. 1 and for different orientations of the adsorbates. The lowest energy structures, where a transition state was found between reactants and products, were then selected for further investigation of the reaction mechanisms and rates. Details of the transition states, adsorption, and co-adsorption energies for the most stable configurations, together with the

![Fig. 1 Different adsorption sites on the Ni(111), Ni(110), and Ni(100) surfaces. A is a top site; B is a bridge site; C is a hcp site; C’ is a fcc site; D is a rectangular fourfold hollow site; D’ is a square fourfold hollow site; E is a long bridge site; F is a short bridge site; G is a pseudo 3-fold hollow site. The color coding for Ni(111) (black), Ni(110) (red), and Ni(100) (blue) surfaces are used throughout this contribution. The Ni atoms are shown in green.](image-url)
structural parameters, are given in Tables S1-S4 in the Supporting information.

Catalytic hydrocarbon combustion

The activation and reaction energies as well as the reaction rate constants calculated at 600 K, which is a typical temperature for synthesis and low temperature catalytic combustion of hydrocarbons [53–55], are given in Table 1 together with results of previous studies when available.

The calculated activation energies for dissociation of CH are 1.15 eV, 0.33 eV, and 0.45 eV on the Ni(111), Ni(110), and Ni(100) surfaces, respectively. The reaction energies are 0.49 eV on the Ni(111) surface, −0.22 eV on the Ni(110) surface and −0.21 eV on the Ni(100) surface. Hence, the reaction is exothermic on the Ni(110) and Ni(100) surfaces while it is endothermic on the Ni(111) surface.

In contrast to dissociation, the lowest activation energy for CH oxidation was obtained on the Ni(111) surface, i.e., 0.85 eV compared to 1.43 eV and 2.46 eV on the Ni(110) and Ni(100) surfaces. The oxidation reaction is exothermic on the Ni(111) surface while it is endothermic on the other surfaces.

The effect of the surface structure on the height of the activation barrier for formyl dissociation to CO and H follows the same order as methylidyne oxidation, and the reaction is exothermic on all surfaces. The activation barriers are 0.15 eV, 0.16 eV, and 0.48 eV for the Ni(111), Ni(110), and Ni(100) surfaces, respectively.

The trends in the relative activation and reaction energies obtained for the Ni(111) and Ni(100) surfaces are similar to those reported previously. Li et al. [57] found a lower barrier for CH dissociation on the Ni(100) surface, i.e., 0.64 eV compared to 1.38 eV on the Ni(111) surface. Blaylock et al. [58] also found similar trends, i.e., 0.91 eV, on the Ni(100) surface compared to 1.40 eV on the Ni(111) surface. The trends of the reaction energies reported in the previous studies are also similar to what is obtained in this work, i.e., the reaction on the Ni(111) surface is endothermic while the reaction on Ni(100) surface is exothermic. It also should be noted that the reaction energy obtained by Wang et al. [24], 1.21 eV, is larger compared to what is reported here since they found different coadsorption sites for C and H. They reported a reaction energy of 0.59 eV for the sum of separated adsorbed species.

Blaylock et al. [58] reported a higher CH oxidation activation energy on the Ni(100) surface, i.e., 2.02 eV, compared to 1.36 eV on the Ni(111) surface and the reaction on both surfaces are endothermic. However, Wang et al. [24] found an exothermic reaction on the Ni(111) surface similar to the present work. The reason for the difference is not clear but it may be due to different adsorption sites investigated. Similar to our results, Zhou et al. [23] obtained a lower CHO to CO and H dissociation barrier on the Ni(111) surface compared to the previous work.

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Ni(100) surface, i.e. 0.18 eV and 0.79 eV, respectively, where both reaction are exothermic.

No results have previously been reported for the Ni(110) surface. The trends observed here (e.g., the effect of the surface structure on the barrier height and reaction energies), as well as those in the “Catalytic hydrocarbon synthesis” section, are discussed in the “Brønsted-Evans-Polanyi principle and reaction profiles” section.

The geometries of the reactants, transition states and products which are presented in Table 1, are shown in Fig. 2. The adsorption and co-adsorption energies, together with the details of these structures, are given in Tables S1, S3, and S4 in the Supporting information.

Catalytic hydrocarbon synthesis

The activation barriers, rate constants at 600 K and reaction energies for hydrocarbon synthesis are given in Table 2.

The highest activation energy for CO dissociation is on the Ni(111) surface, and is 2.99 eV compared to 1.98 eV and 1.83 eV on the Ni(100) and Ni(110) surfaces, respectively. The reaction is endothermic on all three surfaces.

The activation energy for the hydrogenation of CO follows the same order as its dissociation, i.e., it decreases in the order of Ni(111) > Ni(100) > Ni(110). The reaction is endothermic on all surfaces with reaction energies of 1.38 eV, 1.13 eV and 0.88 eV for the Ni(111), Ni(110) and Ni(100) surfaces, respectively.

The barrier of formyl dissociation to CH and O, however, decreases in the order of Ni(100) > Ni(111) > Ni(110). The reaction on the Ni(110) and Ni(100) surfaces is exothermic while it is endothermic on the Ni(111) surface.

The results obtained in the present study are similar to those reported previously (which are shown in Table 2 and are only available for the Ni(111) surface).

Figure 3 shows geometries of the reactants, transition states and products for the reactions given in Table 2. The adsorption and co-adsorption energies together with the details of these structures are given in Tables S2, S3, and S4 in the Supporting information.

Brønsted-Evans-Polanyi principle and reaction profiles

According to the Brønsted-Evans-Polanyi (BEP) principle the activation energy for a given reaction should be linearly proportional to the reaction energy [59, 60]. Figure 4 shows these correlations for the different Ni surface structures studied here (the data used to draw Fig. 4 is provided in Table S5 in the Supporting information). Results from C-H bond breaking/forming are combined in the upper panel and those for C-O bond breaking/forming are shown in the lower panel.

Figure 4 reveals that these reactions support the BEP principle with R² values of 0.85 and 0.72 for C-H and C-O bond breaking/forming and, respectively. However, it should be noted that only three Ni facets have been studied in this work and more facets would improve the statistical relevance of the results.

Including all of the data in a single plot, as done in Fig. S1 (a) in the Supporting information, yields an R²=0.53. This deterioration of the fit to the BEP principle is expected since the chemical species involved in these groups of reactions and also the reactivity of the surfaces are different [61].

The transition state scaling (TSS) method [61, 62], which is related to the BEP principle, correlates the transition state
energy ($E_{TS}$) with either the initial state ($E_{IS}$) or final state ($E_{FS}$) energy (i.e., the energy of the reactants or products). In the present work correlation with the initial state is the same as with the final state since both the forward (bond breaking) and backward (bond forming) reactions are included in the plots. Similar to previous studies [56, 63], correlation between $E_{TS}$ and $E_{FS}$ (shown in Fig. S1 (b) in the Supporting information) yields a larger $R^2$ (0.96) than that obtained in the BEP plot (0.53). This is partly due to the larger energy intervals in the TSS plot compared to the BEP plot [64].

Table 2 The activation energies (eV), reaction rate constants at 600 K (s$^{-1}$), and reaction energies (eV) for the reactions involved in hydrocarbon synthesis$^a$

<table>
<thead>
<tr>
<th>Catalytic hydrocarbon synthesis</th>
<th>CO $\rightarrow$ C + O</th>
<th>CO + H $\rightarrow$ CHO</th>
<th>CHO $\rightarrow$ CH + O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_a$</td>
<td>$k \times 10^{14}$</td>
<td>$\Delta E$</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>2.99</td>
<td>8.20 $\times 10^{-14}$</td>
<td>2.60</td>
</tr>
<tr>
<td>Previous results</td>
<td>3.01$^b$, 2.94$^c$, 3.15$^d$</td>
<td>2.51$^a$</td>
<td>1.35$^b$, 1.48$^c$, 1.47$^d$</td>
</tr>
<tr>
<td>Ni(110)</td>
<td>1.83</td>
<td>2.94 $\times 10^{-4}$</td>
<td>0.76</td>
</tr>
<tr>
<td>Previous results</td>
<td>1.98</td>
<td>1.94 $\times 10^{-5}$</td>
<td>0.82</td>
</tr>
<tr>
<td>Previous results</td>
<td>0.51$^d$</td>
<td></td>
<td></td>
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</tbody>
</table>

$^a$ The activation and reaction energies are ZPVE-corrected values. $^b$ Ref [56] (GGA-PW91 calculations using a 2×2 unit cell and four layer slab). $^c$ Ref [22] (GGA-PW91 calculations using a 3×3 unit cell and four layer slab). $^d$ Ref [24] (GGA-PBE calculations using a 2×2 unit cell and three layer slab).
When hydrogen is co-adsorbed on the Ni surface the CO can react with these atoms instead of dissociating to C + O or desorbing. In this case, CO + H forms CHO. In fact, the activation energies for CHO formation are lower than those for CO dissociation and desorption on all surfaces. The adsorbed CO species is therefore more likely to react with co-adsorbed hydrogen than to dissociate to C and O or to desorb from the surface. These findings are in agreement with the results of temperature programmed desorption experiments done by Andersson et al. [19] in which no CO dissociation was observed on the CO-covered Ni(111) surface. They suggested that the reaction via a formyl species has a barrier below the desorption energy. The preferred formation of CHO could also be the reason why the formation of volatile carbonyls are observed for the Fischer-Tropsch process on Ni [67, 68].

Figure 7 shows the time dependence of the CH concentration produced via the direct dissociation route (CO \[\rightarrow\] C+O followed by C + H \[\rightarrow\] CH) and the formyl route (CO +H \[\rightarrow\] CHO followed by CHO \[\rightarrow\] CH + O) on the three different Ni surfaces. The temperature is 600 K. The data in the Supporting information shows that the desorption energies of the species involved in these reactions are larger than the barriers shown in Figs. 5 and 6. Hence, at moderate pressures all species will be present on the metal surface. Figure 6 shows the average rate of CH formation from each CO molecule on the surface (therefore the concentration of the produced CH increases until it reaches 1). It is evident that both routes are fastest on the Ni(110) surface. Also, the direct route is faster on the Ni(110) and Ni(100) surfaces compared to the formyl route. However, the formyl route will dominate if the Ni(111) surface is used. Similar trends were observed when different H concentrations (between 0.25 and 1.5) were used in the kinetics model.

Since the rate constants (see Table 2) for synthesis reactions are far smaller than those for the combustion reactions (see
Fig. 5 Reaction profiles for catalytic hydrocarbon combustion. Color coding is the same as in Fig. 1.

Fig. 6 Reaction profiles for catalytic hydrocarbon synthesis. Color coding is the same as in Fig. 1.

Fig. 7 Time dependence of the relative concentration of CH produced on Ni(111), Ni(110), and Ni(100) surfaces via direct dissociation (solid lines) and via formyl intermediate (dashed lines). The temperature is 600 K and the initial concentration of adsorbed CO and H are 1 (arbitrary units of concentration). Color coding is the same as in Fig. 1.
Table 1), Ni is a better catalyst for hydrocarbon combustion. This could be the reason for the insensitivity of catalytic activity to the surface structure that has been observed experimentally for FTS reactions [25–27]. It may also be noted that although the transition state theory is expected to be valid when the activation energy is large (since the slow reaction rate will allow for equilibration of vibrational energy in the reactant(s)), it may not be as good as an approximation for some of the faster reactions, such as \( \text{CHO} \rightarrow \text{CH}+\text{O} \) on the Ni(111) and Ni(110) surfaces.

**Conclusions**

The effect of three common nickel surface structures on the reaction energetics of hydrocarbon combustion and synthesis has been systematically examined by DFT calculations using the same models and methods. The results show that the reaction barriers are sensitive to the surface structure. For catalytic hydrocarbon combustion, the CH dissociation barrier is lower compared to its oxidation activation energy on the Ni(110) and Ni(100) surfaces. In contrast, the dissociation barrier is higher on the Ni(111) surface. This means that dissociation is favored on the Ni(110) and Ni(100) surfaces, while oxidation to CHO is favored on the Ni(111) surface. The dissociation barrier increases in the order \( \text{Ni}(110) < \text{Ni}(100) < \text{Ni}(111) \) and the oxidation barrier decreases in the order \( \text{Ni}(100) > \text{Ni}(110) > \text{Ni}(111) \). The barrier for CHO dissociation to CO and H follows the same order as CH oxidation.

For the catalytic hydrocarbon synthesis, the CO dissociation barrier is significantly higher compared to its hydrogenation barrier on all surfaces, which means that hydrogenation to CHO is favored over nickel in the presence of sufficient adsorbed H. This could explain why formation of carbonyls in the nickel-catalyzed Fischer-Tropsch process is observed experimentally [67, 68]. The rate of both reactions decreases in the order \( \text{Ni}(110) > \text{Ni}(100) > \text{Ni}(111) \). For the formyl dissociation to CH and O, the lowest barrier was obtained on the Ni(110) surface. The barrier on the Ni(100) surface is higher compared to the Ni(111) surface, unlike the oxidation and hydrogenation reactions. Also, the barrier for CHO dissociation to CH and O is higher than the dissociation to CO and H. The calculated rate constants at 600 K are rather small for the synthesis process, which could be a reason for the experimental observations that the Fischer-Tropsch process is insensitive to the Ni surface orientation.

Hence, based on DFT calculations, the Ni(110) surface showed a better catalytic activity for hydrocarbon combustion than for hydrocarbon synthesis.

The reactions studied support the BEP relations with R² values of 0.85 for C-H bond breaking/forming and 0.85 for C-O bond breaking/forming. Also the d-band center provides a valid description for the relative catalytic activity of all facets of the Ni surface, except for CH oxidation which is faster on the Ni(111) surface even though the d-band center for this facet is farthest from the Fermi level.

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**References**

Supporting Information

A density functional theory study of hydrocarbon combustion and synthesis on Ni surfaces

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Fax: +46-33-4354008; Address: University of Borås, SE 501-90 Borås, Sweden
Table S1. Adsorption energies (eV) and structural parameters (Å) of the chemical species involved in CH dissociation. The adsorption energies are ZPVE-corrected values. $d_{\text{surf-C}}$ and $d_{\text{surf-H}}$ are the shortest distances between carbon and hydrogen atoms of the adsorbate and any metal atom on the surface.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>$E_{\text{ads}}$</th>
<th>$d_{\text{surf-C}}$</th>
<th>$d_{\text{surf-H}}$</th>
<th>$d_{\text{C-H}}$</th>
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<td>1.698</td>
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<td>C: D' H: D'</td>
<td>– 10.59</td>
<td>1.817</td>
<td>1.811</td>
<td>2.506</td>
</tr>
</tbody>
</table>
**Table S2.** Adsorption energies (eV) and structural parameters (Å) of the chemical species involved in CO dissociation. The adsorption energies are ZPVE-corrected values. $d_{\text{surf-C}}$ and $d_{\text{surf-O}}$ are the shortest distances between carbon and oxygen atoms of the adsorbate and any metal atom on the surface.

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<tr>
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<th>$E_{\text{ads}}$</th>
<th>$d_{\text{surf-C}}$</th>
<th>$d_{\text{surf-O}}$</th>
<th>$d_{\text{C-O}}$</th>
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<tbody>
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<td>Ni(111)</td>
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<td>C: C</td>
<td>−1.89</td>
<td>1.948</td>
<td>---</td>
</tr>
<tr>
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<td>C: D</td>
<td>−1.89</td>
<td>1.875</td>
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<td>Ni(100)</td>
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<td>2.039</td>
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<td>1.213</td>
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<td>Ni(111)</td>
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</tr>
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<td>1.801</td>
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</tr>
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<td>Ni(100)</td>
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<td>1.813</td>
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<td>2.709</td>
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</table>
Table S3. Adsorption energies (eV) and structural parameters (Å and degrees) of the chemical species involved in CHO dissociation to CH and O. The adsorption energies are ZPVE-corrected values. $d_{\text{surf-C}}$ and $d_{\text{surf-O}}$ are the shortest distances between carbon and oxygen atoms of the adsorbate and any metal atom on the surface.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>$E_{\text{ads}}$</th>
<th>$d_{\text{surf-C}}$</th>
<th>$d_{\text{surf-O}}$</th>
<th>$d_{\text{C-H}}$</th>
<th>$d_{\text{C-O}}$</th>
<th>$\theta_{\text{H-C-O}}$</th>
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<tbody>
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<td>C: B O: A</td>
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<td>1.969</td>
<td>1.110</td>
<td>1.289</td>
</tr>
<tr>
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<td>1.807</td>
<td>1.969</td>
<td>1.116</td>
<td>1.257</td>
</tr>
<tr>
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<td>C: B O: B</td>
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<td>1.916</td>
<td>1.960</td>
<td>1.111</td>
<td>1.353</td>
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<td>1.887</td>
<td>1.097</td>
<td>1.820</td>
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<tr>
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<td>C: E O: G</td>
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<td>1.930</td>
<td>1.816</td>
<td>1.121</td>
<td>1.848</td>
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<td>C: B O: B</td>
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<td>1.096</td>
<td>1.958</td>
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<td>CH + O</td>
<td>C: C' O: C'</td>
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<td>1.810</td>
<td>1.100</td>
<td>2.682</td>
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<tr>
<td>Ni(110)</td>
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<td>C: D O: G</td>
<td>−11.89</td>
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<td>1.113</td>
<td>3.704</td>
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<td>1.899</td>
<td>1.922</td>
<td>1.115</td>
<td>3.521</td>
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**Table S4.** Adsorption energies (eV) and structural parameters (Å and degrees) of the chemical species involved in CHO dissociation to CO and H. The adsorption energies are ZPVE-corrected. \(d_{\text{surf-C}}\), \(d_{\text{surf-H}}\) and \(d_{\text{surf-O}}\) are the shortest distances between carbon, hydrogen and oxygen atoms of the adsorbate and any metal atom on the surface.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Site</th>
<th>Site</th>
<th>(E_{\text{ads}})</th>
<th>(d_{\text{surf-C}})</th>
<th>(d_{\text{surf-O}})</th>
<th>(d_{\text{surf-H}})</th>
<th>(d_{\text{C-H}})</th>
<th>(d_{\text{C-O}})</th>
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<td>---</td>
<td>1.110 1.289 117.0</td>
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<td>---</td>
<td>1.111 1.353 112.5</td>
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<tr>
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<td>TS</td>
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<td></td>
</tr>
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<td>TS</td>
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<td>--- 1.796 2.190 1.942</td>
<td>1.159 1.234 122.5</td>
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<td></td>
</tr>
<tr>
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<td>--- 1.875 2.355 1.605</td>
<td>1.306 1.244 114.8</td>
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<tr>
<td>Ni(111)</td>
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<td>C: C H: C'</td>
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<td>2.911 1.191 ---</td>
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Table S5. Activation and reaction energies (eV), as well as energies (eV) of initial (E_{IS}), transition state (E_{TS}) and final (E_{FS}) structures of the species involved in hydrocarbon combustion and synthesis.

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<th>Surface</th>
<th>Surface</th>
<th>E_a(eV)</th>
<th>∆E(eV)</th>
<th>E_{IS}(eV)</th>
<th>E_{TS}(eV)</th>
<th>E_{FS}(eV)</th>
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<td>96.1723</td>
<td>– 95.0223</td>
<td>– 95.6821</td>
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<tr>
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<td>Ni(110)</td>
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<td>– 0.22</td>
<td>–</td>
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<td>– 0.21</td>
<td>–</td>
<td>95.1948</td>
<td>– 94.7453</td>
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<tr>
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<td>Ni(111)</td>
<td>0.15</td>
<td>– 1.38</td>
<td>–</td>
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<td>– 102.7781</td>
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<td>0.16</td>
<td>– 1.13</td>
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<td>– 98.1031</td>
<td>– 99.3947</td>
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<td>1.38</td>
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<tr>
<td>CHO → CH+O</td>
<td>Ni(111)</td>
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<td>0.30</td>
<td>–</td>
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<td>1.86</td>
<td>– 0.59</td>
<td>–</td>
<td>101.8297</td>
<td>– 99.9697</td>
<td>– 102.4247</td>
</tr>
<tr>
<td>C+O → CO</td>
<td>Ni(111)</td>
<td>0.39</td>
<td>– 2.60</td>
<td>–</td>
<td>97.9489</td>
<td>– 97.5590</td>
<td>– 100.5492</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>1.07</td>
<td>– 0.76</td>
<td>–</td>
<td>94.8959</td>
<td>– 93.8245</td>
<td>– 95.6583</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>1.16</td>
<td>– 0.82</td>
<td>–</td>
<td>98.1257</td>
<td>– 96.9652</td>
<td>– 98.9493</td>
</tr>
</tbody>
</table>
Figure S1. Brønsted-Evans-Polanyi (BEP) correlation (a) and the transition state scaling (TSS) relation (b) for all of studied reactions on the Ni(111), Ni(110) and Ni(100) surfaces.
Paper V
DFT study of the water gas shift reaction on Ni(111), Ni(100) and Ni(110) surfaces
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Abstract
Density functional theory (DFT) calculations were used to study the water gas shift (WGS) reaction on Ni(111), Ni(100) and Ni(110) surfaces. The adsorption energy for ten species involved in the reaction together with activation barriers and reaction energies for the nine most important elementary steps were determined using the same model and DFT methods. The results reveal that these energies are sensitive to the surface structure. In spite of this, the WGS reaction occurs mainly via the direct (also referred to as redox) pathway with the CO + O → CO2 reaction as the rate determining step on all three surfaces. The activation barrier obtained for this rate limiting step decreases in the order Ni(110) > Ni(111) > Ni(100). Therefore, if O species are present on the surfaces then the WGS reaction is fastest on the Ni(100) surface. However, the barrier for desorption of H2O (which is the source of the O species) is lower than its dissociation reaction on the Ni(111) and Ni(100) surfaces, but not on the Ni(110) surface. Hence, at low H2O(g) pressures, the direct pathway on the Ni(110) surface will dominate and will be the rate limiting step. The calculations also show that the reason that the WGS reaction does not primarily occur via the formate pathway is that this species is a stable intermediate on all surfaces. The reactions studied here support the Brønsted-Evans-Polanyi (BEP) principles with an R2 value of 0.99.

Keywords: water gas shift reaction, DFT, nickel, Ni(111), Ni(100), Ni(110)

1. Introduction

The water gas shift (WGS) reaction, CO + H2O ⇌ CO2 + H2, is of great importance in many industrial processes, including steam reforming of natural gas, methanation and production of hydrogen. This reaction is also one of the most important reactions in gasification, where carbonaceous materials are converted to gaseous products that can be used to produce energy or other chemicals [1-7]. Different metal catalysts such as Cu, Pt and Au are used to increase the rate of the WGS reaction [8]. Nickel is also widely used since it has a large thermal conductivity, high catalytic conversion and it can be manufactured in different shapes [8-12].

Several experimental and computational studies have focused on the WGS reaction because of its importance. Recent investigations have shown that the WGS reaction mechanism primarily includes the direct, carboxyl and formate pathways [12-15]. Most of the recent studies have focused on the role of the support, on the nature of important intermediates and reactions taking place on the nickel particles and on the nature of the active sites involved in the reaction. Hilaire et al. [16] proposed that the reaction occurs via a direct pathway on Ni/CoO2 surfaces, where CO2
is produced via the direct oxidation of CO. Grenoble et al. [17] suggested a mechanism which proceeds via formic acid formation over acidic sites on an Al₂O₃ surface. This formic acid intermediate subsequently decomposes to CO₂ and H₂. Sanchez-Escribano et al. [18] observed the presence of formate species on Ni/Al₂O₃ surfaces using FTIR spectroscopy. Based on diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies on Ni/CoO₂ catalysts, Jacobs et al. [19] suggested a mechanism where formate is formed over Ce sites. Formate was also observed on the Ni(110) surface using high resolution electron energy loss spectroscopy (HREELS) by Vesselli et al. [20] and Wambach et al. [21]. Dehydration of formic acid on Ni(110) and Ni(110)(4×5)C surfaces was studied using HREELS by Madix et al. [22]. They observed formate on the carbide surface and a mixed adlayer of CO and HCOO on the pure Ni surface. Infrared reflection absorption spectroscopy (IRAS) was employed by Yamakata et al. [23] to investigate the dehydration of formate adsorbed on a Ni(110) surface. They proposed a surface reaction mechanism which includes unimolecular dehydrogenation of formate and suggested that the rate determining step of the dehydrogenation reaction is the C-H bond dissociation.

Experimental studies have been complemented by theoretical calculations. However, only two of these have studied the mechanism of the WGS reaction on Ni surfaces [12, 15]. Most of the computational studies that have been performed on similar systems have focused, instead, on methanol synthesis [24], methane reforming [25-27], trends of the WGS reaction over a variety of transition metals [15, 28, 29], methanation of CO [25, 30], effects of co-adsorbed molecules and step defects on the reactivity of CHₓ species [25, 31, 32], and formate adsorption and decomposition on Ni surfaces [20, 33-35].

One of the two studies that investigated the mechanism of the WGS reaction on a Ni surface was performed by Lin et al. [15]. They used DFT calculations to investigate the WGS reaction on a series of transition metals including the Ni(111) surface, and their results are compared with the present calculations below. The other study was done by Catapan et al. [12], where DFT was used to study the reaction on Ni(111) and Ni(221) surfaces. They found that the Ni(111) surface is a better catalyst for the WGS reaction, which occurs mainly via the carboxyl pathway with the CO + OH → COOH reaction as the rate determining step. They also suggested that a parallel route via formate and formyl intermediates is favored on the Ni(221) surface.

The WGS reaction mechanism has also been investigated on other surfaces using DFT [36-38] calculations. For example, a DFT study together with experimental data for the WGS reaction catalyzed by Pt were provided by Grabow et al. [39]. They predicted that the most important reaction channel proceeds via a carboxyl intermediate while formate acts only as a spectator. Furthermore, Fajín et al. [40] studied the role of step sites in the WGS reaction catalyzed by Cu, and found that the associative route through the carboxyl intermediate is favored in the presence of the steps. Bunluesin et al. [36] determined the steady-state WGS kinetics on ceria-supported Pd, Pt and Rh catalysts and found that the ceria structure significantly affects the results. The promotional effect of alkali additives (Na, Li and K) on the WGS reaction for Pt/Al₂O₃ and Pt/TiO₂ catalysts was investigated by Pazmiño et al. [38]. They found that the active platinum remains in the metallic state and that the promotion by alkali is due to the modification of the support properties.

The experimental and computational studies presented above show that the details of the WGS reaction mechanism are not fully understood. In fact, there are some inconsistencies between
experimental and computational results, such as the role of formate species. To address these inconsistencies, a systematic DFT study of the WGS reaction on Ni(111), Ni(100) and Ni(110) surfaces was performed using the same methods and models. The present contribution extends previous investigations by performing a comparative study of the WGS reaction on these three surfaces and identifying the most important reaction pathways. To the best of our knowledge, this is the first time that the WGS reaction on these three crystallographic surface orientations has been studied using the same computational models and methods. These results are expected to aid in identifying which of the three crystallographic surfaces is the most efficient for the WGS reaction, which pathway is favored, and the detailed mechanisms of the WGS reaction on these surfaces.

2. Theory

2.1. Methods

The Vienna ab initio simulation package (VASP) was used for the calculations [41-44]. Spin polarized DFT was used with the generalized gradient approximation and the Perdew, Burke and Ernzerh (GGA-PBE) [45] functional. The Kohn-Sham equations were solved using the projector-augmented wave method (PAW) [46, 47] with a 4×4×1 Monkhorst-Pack grid of k-points [48] for the numerical integration in reciprocal space. The Kohn-Sham orbitals were expanded in a plane-wave basis set using a kinetic energy cut off of 400 eV. Larger cut offs and finer k-meshes were also examined and yielded the same trends as reported below.

The conjugate-gradient (CG) method was used for geometry optimizations, and the minimum energy structure was identified when the change in the total energy and the forces acting on each ion became smaller than 10^{-5} eV and 10^{-3} eVÅ^{-1}, respectively. The transition states were located using the climbing image-nudged elastic band method (CI-NEB) [49, 50], where six images were placed between the reactant and product geometries. A –5.0 eVÅ^{-2} spring force constant between images was used to relax them until the maximum force acting on each ion was less than 0.1 eVÅ^{-1}. Calculations using a stricter force convergence criterion of 0.01 eVÅ^{-1} changed the activation energy by less than 0.2 meV.

Using the same convergence criteria, the dimer approach [51] was also employed to locate the transition states for R4 and R8 on the Ni(111) surface, R8 and R9 on the Ni(100) surface and R4 on the Ni(110) surface (see Section 2.3). In this method, the most stable configuration of the reactant molecule on the surface is determined using a standard minimization method before searching for a nearby saddle point. The dimer method was used for these elementary steps since it converged to the TS structure in a more computationally efficient way compared to the CI-NEB method.

Vibrational frequencies were calculated using ionic displacements of 0.01 Å. Only the adsorbates were allowed to move, and the frequencies were obtained by diagonalizing the finite difference Hessian matrix. The calculations confirmed that the stationary structures were minimum energy
geometries (zero imaginary frequencies) or transition states (one imaginary frequency). The vibrational frequencies were also used to determine the zero point vibrational energies (ZPVEs). This method has been successfully used in previous studies of similar systems [52-54].

2.2. Supercell and adsorption sites

Semi-infinite Ni crystal surfaces were modelled using periodic boundary conditions based on a four-layer slab with a 2×2 unit cell. The periodic conditions were applied along the x and y axes, and a 10 Å vacuum separated the surfaces in the z direction. In order to maintain the bulk crystal structure the two bottom layers of the slab were fixed and the two upper layers were free to relax. This slab size corresponds to a 1/4 and 1/2 monolayer coverage when there are one or two adsorbates, respectively, on the surface. This unit cell size yields converged results in a computationally feasible time and is commonly used in investigations of similar systems [12, 55-59]. Earlier studies have also shown that similar trends are obtained at lower surface coverages [60]. The different surface sites that are present on the Ni(111), Ni(100) and Ni(110) surfaces and that were investigated are shown in Figure 1.

It may be noted that adsorption of some species, e.g., CO, O and C induce reconstruction of the Ni(110) and Ni(100) surfaces [61-65]. For instance, scanning tunneling microscopy [61] and photoelectron diffraction [65] measurements showed that the Ni(100) surface is reconstructed at high C coverages. However, these are at coverages that are higher than those studied here and the exact structure (at the atomic level) is not known. Thus, as a starting point we use the pure nickel to model the catalytic surfaces as has been done previously [12, 37, 66-68]. Future work may focus on the reconstructed surfaces.

Figure 1. Different adsorption sites on the Ni(111), Ni(100) and Ni(110) surfaces. A is a top site; B is a bridge site; C is a hcp site; C’ is a fcc site; D is a rectangular 4-fold hollow site; D’ is a square 4-fold hollow site; E is a long bridge site; F is a short bridge site; G is a pseudo 3-fold hollow site.
The adsorption energies ($E_{ads}$) are $E_{ads} = E_{surf+adsorbate} - E_{surf} - E_{adsorbate}$ where $E_{surf+adsorbate}$ is the total energy of the geometry optimised surface-adsorbate(s) system, $E_{surf}$ is the total energy of the geometry optimised surface and $E_{adsorbate}$ is the total energy of the isolated, geometry optimized adsorbate(s) in vacuum.

2.3. Elementary steps

The following nine elementary steps were studied. They are the water dissociation (R1 and R2) together with three different pathways for CO oxidation to CO$_2$, namely the direct path (R3), the carboxyl path (R4 and R5) and the formate path (R6, R7 and R8), and finally formation of hydrogen (R9). These are the most important elementary steps and have previously been used to investigate the WGS reaction [12, 15, 28, 37].

\[
\begin{align*}
\text{H}_2\text{O} & \rightleftharpoons \text{OH} + \text{H} & \text{(R1)} \\
\text{OH} & \rightleftharpoons \text{O} + \text{H} & \text{(R2)} \\
\text{CO} + \text{O} & \rightleftharpoons \text{CO}_2 & \text{(R3)} \\
\text{CO} + \text{OH} & \rightleftharpoons \text{COOH} & \text{(R4)} \\
\text{COOH} & \rightleftharpoons \text{CO}_2 + \text{H} & \text{(R5)} \\
\text{CO} + \text{H} & \rightleftharpoons \text{CHO} & \text{(R6)} \\
\text{CHO} + \text{O} & \rightleftharpoons \text{HCOO} & \text{(R7)} \\
\text{HCOO} & \rightleftharpoons \text{CO}_2 + \text{H} & \text{(R8)} \\
\text{H} + \text{H} & \rightleftharpoons \text{H}_2 & \text{(R9)}
\end{align*}
\]

3. Results and discussion

3.1. Adsorption energies

Geometry optimizations were performed for all adsorption sites shown in Figure 1 and for different orientations of the adsorbates. The lowest energy structures were then selected for investigations of the reaction mechanism. The lowest energy structures of the individual chemical species involved in the WGS reaction are shown in Figure 2 and are presented in Table 1. Results from previous theoretical studies are also included in the table. Details of the structures of the most stable configurations are given in the Tables S1-S10 in the Supporting Information.
It is widely accepted that adsorbates bind more strongly to high symmetry sites than to low symmetry sites, and to atoms with low coordination numbers rather than high coordination numbers [69-71]. The surface metal atom coordination numbers for the Ni(111), Ni(100) and Ni(110) surfaces are 9, 8 and 7, respectively, and one would therefore expect the strongest adsorption on the Ni(110) surface. In addition, it has previously been shown that all of the adsorbates are more negatively charged than when they are in the vacuum [60]. This extra electron density is assumed to come from the frontier d orbitals of the metal surface. The intensities of the occupied orbitals at the Fermi level for the Ni(111), Ni(100) and Ni(110) surfaces are 2.0, 2.2 and 2.7 states/eV, respectively [72] and therefore the Ni(110) surface can donate a higher electron density to the adsorbate. Hence, based on both the differences in electron density and coordination number, one would expect that the strength of the adsorption energies would decrease in the order Ni(110) > Ni(100) > Ni(111). The results in Table 1 are consistent with these general trends since five of the ten species adsorb most strongly on the Ni(110) surface and the other five absorb most strongly on the Ni(100) surface. This is discussed in more detail below.

<table>
<thead>
<tr>
<th></th>
<th>H$_2$O</th>
<th>OH</th>
<th>CO$_2$</th>
<th>COOH</th>
<th>CHO</th>
</tr>
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<tr>
<td>Ni(111)</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
<td><img src="image5" alt="Image" /></td>
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<tr>
<td>Ni(110)</td>
<td><img src="image11" alt="Image" /></td>
<td><img src="image12" alt="Image" /></td>
<td><img src="image13" alt="Image" /></td>
<td><img src="image14" alt="Image" /></td>
<td><img src="image15" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 2. The top and the side views of the lowest energy structures of the adsorbed species on the Ni(111), Ni(100) and Ni(110) surfaces.
Table 1. Adsorption energies (eV) and adsorption sites of the chemical species involved in the WGS reaction.

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface</th>
<th>Site</th>
<th>$E_{ads}$</th>
<th>Previous results for $E_{ads}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>H$_2$O</strong></td>
<td>Ni(111)</td>
<td>O: A</td>
<td>-0.19</td>
<td>-0.29, -0.47, -0.32, -0.17, -0.25</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>O: A</td>
<td>-0.27</td>
<td>-0.26</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>O: G</td>
<td>-0.40</td>
<td>-0.54</td>
</tr>
<tr>
<td><strong>OH</strong></td>
<td>Ni(111)</td>
<td>O: C’</td>
<td>-3.10</td>
<td>-2.98, -3.42, -3.34, -3.31, -3.14</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>O: D’</td>
<td>-3.30</td>
<td>-3.36, -3.26, -3.57</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>O: F</td>
<td>-3.48</td>
<td></td>
</tr>
<tr>
<td><strong>CO$_2$</strong></td>
<td>Ni(111)</td>
<td>C: B</td>
<td>-0.03$^*$</td>
<td>-0.12, -0.02, +0.31, +0.03</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>C: A</td>
<td>-0.06</td>
<td>-0.08</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>C: F</td>
<td>-0.25</td>
<td>-0.32, -0.22</td>
</tr>
<tr>
<td><strong>COOH</strong></td>
<td>Ni(111)</td>
<td>C: A</td>
<td>-2.17</td>
<td>-2.25, -2.26, -2.54, -1.99</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>C: B</td>
<td>-2.70</td>
<td>-2.62</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>C: E</td>
<td>-2.55</td>
<td></td>
</tr>
<tr>
<td><strong>CHO$^{[23]}$</strong></td>
<td>Ni(111)</td>
<td>C: B, O: A</td>
<td>-2.19</td>
<td>-2.49, -2.41, -2.26, -1.99</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>C: B, O: B</td>
<td>-2.76</td>
<td>-3.15, -2.51</td>
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<tr>
<td></td>
<td>Ni(110)</td>
<td>C: F, O: A</td>
<td>-2.42</td>
<td></td>
</tr>
<tr>
<td><strong>HCOO$^{[23]}$</strong></td>
<td>Ni(111)</td>
<td>O$_1$: A, O$_2$: A</td>
<td>-2.69</td>
<td>-0.86, -3.02, -2.80</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>O$_1$: A, O$_2$: B</td>
<td>-2.88</td>
<td>-1.07, -3.27</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>O$_1$: A, O$_2$: A</td>
<td>-3.29</td>
<td>-1.60, -3.42</td>
</tr>
<tr>
<td><strong>H$_2$</strong></td>
<td>Ni(111)</td>
<td>A</td>
<td>-0.17</td>
<td>-0.22, -1.17</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>A</td>
<td>-0.22</td>
<td>-1.09</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>A</td>
<td>-0.33</td>
<td>-0.89</td>
</tr>
<tr>
<td><strong>CO$^{[24]}$</strong></td>
<td>Ni(111)</td>
<td>C: C</td>
<td>-1.89</td>
<td>-3.05, -2.85, -1.56, -2.32</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>C: D’</td>
<td>-1.96</td>
<td>-3.04, -1.53, -2.26</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>C: F</td>
<td>-1.89</td>
<td>-1.42, -3.42, -1.58</td>
</tr>
<tr>
<td><strong>O</strong></td>
<td>Ni(111)</td>
<td>C’</td>
<td>-5.30</td>
<td>-5.49, -5.14, -4.81, -5.50</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>D’</td>
<td>-5.62</td>
<td>-6.97, -5.38</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>E</td>
<td>-4.97</td>
<td>-5.49</td>
</tr>
<tr>
<td><strong>H</strong></td>
<td>Ni(111)</td>
<td>C’</td>
<td>-2.65</td>
<td>-2.80, -2.81, -2.78, -2.77</td>
</tr>
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<td>Ni(100)</td>
<td>D’</td>
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<td></td>
<td>Ni(110)</td>
<td>G</td>
<td>-2.51</td>
<td>-0.45, -0.37</td>
</tr>
</tbody>
</table>

* The adsorption energies are ZPVE-corrected values. $^b$ Reference [75] (GGA-PBE calculations using a 2×2 unit cell and three layer slab). $^c$ Reference [52] (GGA-PW91 calculations using a 2×2 unit cell and four layer slab). $^d$ Reference [76] (GGA-PBE calculations using a 3×2 unit cell and three layer slab). $^e$ Reference [12] (GGA-PBE calculations using a 2×2 unit cell and four layer slab). $^f$ Reference [27] (GGA-PBE calculations using a 3×3 unit cell and four layer slab). $^g$ Reference [68] (GGA-PBE calculations using a 3×2 unit cell and three layer slab). $^h$ Reference [55] (GGA-PBE calculations using a 2×2 unit cell and three layer slab). $^i$ Reference [20] (GGA-PBE calculations using a 3×2 unit cell and five layer slab). $^j$ Reference [71] (GGA-PBE calculations using a 3×2 unit cell and three layer slab). $^k$ Reference [58] (GGA-PBE calculations using a 2×2 unit cell and four layer slab). $^l$ Reference [77] (GGA-PBE calculations using a 2×2 unit cell and four layer slab). $^m$ Reference [78] (GGA-PW91 calculations using a 2×2 unit cell and four layer slab). $^n$ Reference [79] (GGA-PW91 calculations using a 1×1 unit cell and five layer slab). $^o$ Reference [59] (GGA-PW91 calculations using a 2×2 unit cell and four layer slab). $^p$ Reference [80] (GGA-PW91 calculations using a 2×2 unit cell and four layer slab). $^q$ Reference [81] (GGA-PBE calculations using a 2×2 unit cell and four layer slab). $^r$ Reference [82] (GGA-PBE calculations using a 2×2 unit cell and five layer slab). $^s$ Reference [83] (GGA-PW91 calculations using a 3×3 unit cell and three-four layer slab). $^t$ Reference [20] (GGA-PBE calculations using a 3×2 unit cell and three-four layer slab). $^u$ This is the value before ZPVE corrections.
As shown in Table 1, water binds most strongly to the Ni(110) surface and the adsorption is via its oxygen atom on top of a Ni atom on all surfaces. This is similar to previous DFT results [12, 52, 58]. The adsorbed water molecule is tilted near parallel with the surface, which is in agreement with earlier experimental observations for Ni(110) [84-86] and Ni(111) surfaces [87]. Pangher et al. [86] used polarization-dependent surface-extended X-ray-absorption fine-structure to study the structure of water adsorbed on the Ni(110) surface. They reported that water is adsorbed via its O atom in a top site with a nearest-neighbor O-Ni separation of 2.06 Å. This is comparable to the 2.12 Å obtained in this work (see Table S1). We also obtained vibrational frequencies of 3713, 1584 and 3828 cm\(^{-1}\) for the symmetric stretching, bending, and the asymmetric stretching of the water molecule, which compare well with the experimental values of 3657, 1595 and 3756 cm\(^{-1}\) obtained by Tennyson et al. [88].

It may be noted that the present calculations were performed with the standard DFT-GGA approach which is known to give accurate descriptions of the relevant systems [12, 15, 26, 37, 40, 52, 53, 68, 75, 77, 89-91]. However, this approach does not include dispersion forces, which are expected to affect the absolute binding energies, especially for weakly adsorbed species such as H\(_2\)O and CO\(_2\). The DFT-GGA binding energies for H\(_2\)O and CO\(_2\) presented here may therefore significantly underestimate the real binding energies. For example Dietz et al. [92] included the dispersion forces in their DFT calculations and obtained an adsorption energy of −0.27 eV for CO\(_2\) on the Ni(111) surface compared to −0.03 eV obtained here. However, it is important to note that these differences do not affect the conclusions presented in this study.

Similarly to water, OH binds most strongly to the Ni(110) surface and the adsorption is via the oxygen atom. The calculated O-H and OH-surface stretching frequencies on the Ni(110) surface are 3659 and 437 cm\(^{-1}\), respectively, which are in good agreement with the experimental values of 3580 and 450 cm\(^{-1}\) obtained using HREELS [93]. Also, experimental observations predicted that the OH is inclined on the Ni(110) surface which is consistent with the structure obtained here [93]. The adsorption energies obtained for OH agree with those previously obtained from theoretical studies (see Table 1). However, the values are higher than the activation energies (1.17-1.78 eV) observed experimentally for OH desorption from polycrystalline nickel [94]. The reason for this discrepancy is not known.

According to DFT-GGA, the CO\(_2\) molecule does not bind strongly to the Ni(111) and Ni(100) surfaces (although, as discussed above, dispersion forces are not included), and slightly different adsorbate structures are found on the three surfaces. When it is initially placed close to and parallel to the Ni(111) surface (initial surface-CO\(_2\) separations from 3 to 7 Å were studied) it moves away from the surface during geometry optimization. An adsorption energy of −0.03 eV was calculated for this surface. It should be noted that this value is without ZPVE corrections since two imaginary frequencies were found for the adsorbed structure. However, the ZPVE corrections do not affect the activation barrier for the production of CO\(_2\) (the only reaction that includes single CO\(_2\) species, i.e., R3), and the effect on the reaction and adsorption energies is not significant since both modes have very low frequencies. It can also be noted that a second stable structure for CO\(_2\) (with no imaginary frequencies) was found on the Ni(111) surface where carbon dioxide has a bent geometry with the carbon atom pointing towards the surface. However, this structure has an adsorption energy of +0.25 eV, which shows that it is a local minimum energy site (endothermic adsorption). This is similar to the results obtained by Dietz et al. [92]. They included the dispersion forces in their DFT calculations and reported that CO\(_2\) is weakly
interacting with the Ni(111) surface with an adsorption energy of \(-0.27\) eV (compared to \(-0.03\) eV obtained here). They also found a metastable structure where the adsorbed CO\(_2\) is bent with an O-C-O angle of 133° (compared to 138° obtained here for the second stable structure). This metastable structure has an adsorption energy of \(-0.07\) eV (compared to \(+0.25\) eV obtained here). Wang et al. [55] also found a similar structure with a positive adsorption energy. The results of the weakly adsorbed structures (and not of the local minimum energy site) are more relevant to the current studies and are therefore reported here. In addition, it can be noted that the reaction to produce the CO\(_2\) at both of these adsorption sites has the same transition state structure (which is investigated in Section 3.3). Therefore the reaction dynamics is the same irrespective to which product is selected. Similarly to the results reported here, Catapan et al. [12] and Zhu et al. [27] found a small exothermic adsorption energy for CO\(_2\) on the Ni(111) surface. Zhu et al. also reported physisorbed CO\(_2\) on the Ni(111) surface with an energy of \(-0.02\) eV. The physisorbed structure on the Ni(111) surface is also consistent with experimental observations by Heiland et al. [95] where they used fast ion beam and fast molecular beam techniques to investigate CO\(_2\) dissociation on this surface. They did not detect any chemisorbed CO\(_2\) on this surface at low temperatures. The adsorption energy on the Ni(110) surfaces is \(-0.25\) eV. Experimental observations also support the results presented here since the Ni(110) surface is the only transition metal low Miller index surface to which CO\(_2\) chemically binds under Ultra High Vacuum (UHV) conditions [96, 97].

A slightly different geometry is obtained for CO\(_2\) when it is physisorbed on the Ni(100) and Ni(110) surfaces. It has a bent geometry on both of these surfaces with the carbon atom pointing towards the surface. The CO\(_2\) is adsorbed on the short-bridge site on the Ni(110) surface with the molecular plane perpendicular to the surface. This is consistent with previous experimental and theoretical observations [20, 96].

The binding energies for COOH and CHO are largest on the Ni(100) surface. The reason that they bind stronger to this surface than the Ni(110) surface could be due to the orientation of these molecules on the surface. For CHO on the Ni(100) surface, the C-O bond is almost parallel to the surface, whereas the carbon atom points towards the surface on the other two surfaces. The angle between the C-O bond and the surface plane is 5.6, 10.7 and 16.1 degrees on the Ni(100), Ni(110) and Ni(111) surfaces, respectively. For COOH, the angle between the C-O\(_1\) bond (see Figure 2) and the surface plane is 2.5, 4.5 and 5.7 degrees on the Ni(100), Ni(110) and Ni(111) surfaces, respectively. Zhou et al. [68] found similar trends for CHO adsorption and reported adsorption energies of \(-2.41\) and \(-3.15\) eV on Ni(111) and Ni(100) surfaces, respectively.

The formate intermediate binds strongest to the Ni(110) surface and is adsorbed via its two oxygen atoms on all three surfaces. Experimental studies support these results since the bidentately adsorbed formate is the species that is observed in high concentrations [15]. On the Ni(111) and the Ni(110) surfaces, both oxygen atoms are adsorbed on the top sites with similar distances while on the Ni(110), one oxygen atom (O\(_2\) in Figure 2) is on top site and the other one (O\(_1\) in Figure 2) is on the bridge site and is closer to the surface. The O-C-H angles are similar on both Ni(111) and Ni(110) surfaces but not on the Ni(100) surface. The O-C-O angle follows the same order as the adsorption energy, i.e., Ni(110) > Ni(100) > Ni(111).

The experimentally observed vibrational frequencies for HCOO on Ni(110) reported by Haq et al. [98] are in good agreement with those calculated in this work. They observed bidentately adsorbed HCOO and reported 2840 cm\(^{-1}\) as the C-H bond stretching frequency (compared to
2961 cm\(^{-1}\) (calculated here), 1600 cm\(^{-1}\) for the asymmetric vibration of the O-C-O bond (compared to 1504 cm\(^{-1}\) calculated here), 1352 cm\(^{-1}\) for the O-C-O symmetric vibration (compared to 1296 cm\(^{-1}\) calculated here), 1384 cm\(^{-1}\) for the H-C-O angle vibration (compared to 1344 cm\(^{-1}\) calculated here), 1000 cm\(^{-1}\) for the C-H wagging vibration (compared to 961 cm\(^{-1}\) calculated here) and 770 cm\(^{-1}\) as the frequency for the H-C-O angle (compared to 710 cm\(^{-1}\) calculated here). A C-O-C angle of 129.8\(^{\circ}\) was obtained on the Ni(110) surface, which is similar to that reported in XPD measurements (124\(^{\circ}\)) by Emundts et al. [99]. Pang et al. [71] used DFT to calculate HCOO adsorption energies of –0.86, –1.07 and –1.60 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. They defined the binding energy with respect to the gas phase CO\(_2\) and \(\frac{1}{2}\)H\(_2\) molecules. Using the same method we obtain adsorption energies of –0.46, –0.65 and –1.06 eV for the Ni(111), Ni(100) and Ni(110) surfaces, respectively, which has similar trends compared to their results. However the values are about 0.5 eV lower. The reason for the discrepancy between those results and the data presented here could be the larger unit cell that they used in their calculations, and thus their calculated binding energies are expected to be lower than the values obtained in this study. In this work, the energy calculated for isolated CO\(_2\) is –22.67 eV and for H\(_2\) it is –6.76 eV.

The hydrogen molecule binds to the top site, A, on all surfaces and binds strongest to the Ni(110) surface. The adsorption energies are smaller than those calculated by Wang et al. [77]. This is expected since they defined the binding energy of H\(_2\) as \(E_{\text{ads of hydrogen}} = 2E_{\text{H/slab}} - [E_{\text{Hydrogen}} + 2E_{\text{slab}}]\), where \(E_{\text{H/slab}}\) is the total energy of the slab with the chemisorbed atomic H on the surface, \(E_{\text{Hydrogen}}\) is the energy of the H\(_2\) molecule and \(E_{\text{slab}}\) is the energy of the slab. They reported adsorption energies of –1.17, –1.09 and –0.89 eV for hydrogen on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. Using their method we obtain adsorption energies of –1.15, –1.11 and –0.82 eV for the Ni(111), Ni(100) and Ni(110) surfaces, respectively. These numbers are also in good agreement with previously reported experimental data, i.e. –1.00, –1.00 and –0.93 eV for the Ni(111), Ni(100) and Ni(110) surfaces, respectively [77, 100].

CO binds to the surface via its carbon atom and the binding energy is insensitive to the surface geometry. This is similar to experimental observations by Stuckless et al. [101]. They used calorimetry and obtained adsorption energies of –1.35, –1.27 and –1.37 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. Calculated heats of adsorption in this work are about 0.5 eV higher than the experimental values. This difference may be due to the inability of the PBE functional to accurately predict CO binding energies [81]. Binding energies calculated with the alternative revised version of the PBE functional, RPBE [81], by Blaylock et al. [58] are closer to the experimental values. Both Blaylock et al. [58] and Zhou et al. [68] calculated a slightly higher adsorption energy on the Ni(111) surface than on Ni(100). However, the trends observed here are similar to those obtained by Hammer et al. [81]. The lowest energy adsorption site for CO on the Ni(110) surface was on the short bridge site which agrees with experimental observations by Zhao et al. [102]. They used low-energy electron diffraction (LEED) to measure a Ni-C distance of 1.85 Å and a C-O bond length of 1.15 Å for the adsorbed CO, which are in good agreement with our results, i.e., 1.87 Å and 1.18 Å, respectively (see Table S10). The highest adsorption energy on the Ni(111) surface is in the three fold coordinated hollow site, C, which is consistent with the surface-extended x-ray-absorption fine structure (SEXAFS) studies by Becker et al. [103]. They also reported a C-O bond length of 1.19 Å for the adsorbed carbon monoxide, which is the same as that calculated here (see Table S10).
Oxygen and hydrogen bind stronger to the Ni(100) surface than to the other surfaces. The trends obtained here are in agreement with previous calculations. In agreement with our results, Fajín et al. [52] reported a stronger adsorption of oxygen on the Ni(111) (−5.60 eV) than on the Ni(110) (−5.49 eV) surfaces. Similarly, Blaylock et al. [58] obtained adsorption energies of −4.81 and −5.46 eV for the Ni(111) and Ni(100) surfaces, respectively. The trends of oxygen adsorption energies are also similar to experimental adsorption energies reported by Hammer et al. [81], i.e., −4.84 and −5.41 eV for the Ni(111) and Ni(100) surfaces, respectively.

The adsorption energies for the H atom are similar to those reported previously, except for the values calculated by Kresse et al. [59] and Bhatia et al. [80] which are far lower. This is because they used half of the hydrogen molecule (H₂) energy as the energy of the isolated adsorbate. Kresse et al. calculated adsorption energies of −0.60, −0.57 and −0.45 eV, and Bhatia et al. obtained −0.49, −0.55 and −0.37 eV for hydrogen atom adsorption on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. Using the same method we obtain adsorption energies of −0.52, −0.57 and −0.37 eV for the Ni(111), Ni(100) and Ni(110) surfaces, respectively, which are similar to their energies. In this work, the energy calculated for isolated H₂ is −6.76 eV and for atomic H it is −1.12 eV.

Christmann et al. [104] used low energy electron diffraction (LEED), thermal desorption spectroscopy (TDS) and work function measurements to study hydrogen atoms on the Ni(111) surface. They observed that H atoms occupy the three fold hollow site with a Ni-H bond length of 1.84 Å. This is in agreement with the value of 1.71 Å calculated here (see Table S10). The vibrational frequency obtained here for H at the three-fold site on the Ni(111) surface is 1159 cm⁻¹, which is similar to the value of 1137 cm⁻¹ obtained from neutron inelastic-scattering measurements [105]. Also, the calculated adsorption energy and Ni-H distance for the Ni(100) surface, i.e., 2.70 eV and 1.84 Å, agree well with previously reported experimental values of 2.80 eV and 1.82-1.84 Å [106].

### 3.2. Co-adsorption energies

The initial structures for the geometry optimizations of co-adsorbed species were obtained by placing the individual adsorbates in their minimum energy sites (shown in Figure 1). These structures were then geometry optimized, and the resulting structures with lowest energy were used to investigate the reaction mechanism. This method has been used successfully before [73, 74]. It may be noted that for some structures other co-adsorption sites were examined. However, in all cases, these structures yielded higher (less negative) total energies compared to that of the co-adsorbed species placed in their individual minimum energy sites.

The results are presented in Tables S1-S9 in the Supporting Information. Except for the oxygen on the Ni(110) surface, the co-adsorption sites are the same as those found for the isolated adsorbates. The adsorption energy for oxygen on the Ni(110) surface is the strongest at the long bridge site E, whereas the co-adsorbed O shifts from the E site to the G site for all combinations of co-adsorbed species that include an O atom.
3.3. Transition states and reaction energies

The activation and reaction energies of all the elementary steps (R1-R9) are summarized in Figure 3 and Table 2 together with the results from previous theoretical studies. Details of the structures of the reactants, products and transition states are given in the Supporting Information (Tables S1-S9 and Figures S1-S9).

Table 2. The activation and reaction energies (eV) and imaginary frequency (cm\(^{-1}\)) for the elementary steps of the WGS reaction.\(^a\) The data for R7 are taken from our previous study [73]. The activation and reaction energies are for the forward reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Surface</th>
<th>Ea(eV)</th>
<th>∆E(eV)</th>
<th>Freq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1: H(_2)O ⇌ OH + H</td>
<td>Ni(111)</td>
<td>This work</td>
<td>0.67</td>
<td>−0.20</td>
</tr>
<tr>
<td></td>
<td>Ni(111)</td>
<td>Previous studies</td>
<td>0.90(^b), 0.79(^c), 0.71(^d), 0.92(^f)</td>
<td>−0.28(^b), −0.10(^c), −0.25(^e)</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>This work</td>
<td>0.76</td>
<td>−0.63</td>
</tr>
<tr>
<td></td>
<td>Ni(100)</td>
<td>Previous studies</td>
<td>0.40(^d), 0.74(^e)</td>
<td>−0.49(^d)</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>This work</td>
<td>0.38</td>
<td>−0.56</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>Previous studies</td>
<td>0.39(^d)</td>
<td>−0.52(^d)</td>
</tr>
<tr>
<td>R2: OH ⇌ O + H</td>
<td>Ni(111)</td>
<td>This work</td>
<td>0.79</td>
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<td></td>
<td>Ni(111)</td>
<td>Previous studies</td>
<td>0.85(^b), 1.09(^d), 0.85(^f)</td>
<td>−0.20(^b), 0.03(^f), −0.34(^e), −0.15(^c)</td>
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</tr>
<tr>
<td></td>
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<td>−0.31(^b)</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
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<td>0.61</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>Previous studies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R3: CO + O ⇌ CO(_2)</td>
<td>Ni(111)</td>
<td>This work</td>
<td>1.35</td>
<td>0.65(^*)</td>
</tr>
<tr>
<td></td>
<td>Ni(111)</td>
<td>Previous studies</td>
<td>1.53(^d), 1.40(^e), 1.54(^d)</td>
<td>0.73(^e), 0.28(^d), 0.96(^d)</td>
</tr>
<tr>
<td></td>
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<td>This work</td>
<td>1.25</td>
<td>1.15</td>
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<td>Previous studies</td>
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<td></td>
<td>Ni(110)</td>
<td>This work</td>
<td>1.57</td>
<td>0.72</td>
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<td></td>
<td>Ni(110)</td>
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<tr>
<td>R4: CO + OH ⇌ COOH</td>
<td>Ni(111)</td>
<td>This work</td>
<td>1.30</td>
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<td></td>
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<td>1.73</td>
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<td>Previous studies</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni(110)</td>
<td>This work</td>
<td>1.44</td>
<td>1.18</td>
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<tr>
<td></td>
<td>Ni(110)</td>
<td>Previous studies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R5: COOH ⇌ CO(_2) + H</td>
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<td>This work</td>
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<td>−0.02</td>
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<td>Previous studies</td>
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<td>−0.52(^e), 0.08(^d)</td>
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<tr>
<td></td>
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<td>This work</td>
<td>1.21</td>
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<td>This work</td>
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<td>−0.16</td>
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<td></td>
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<td>Previous studies</td>
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<tr>
<td>R6: CO + H⇌ CHO</td>
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<td>This work</td>
<td>1.53</td>
<td>1.38</td>
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<tr>
<td></td>
<td>Ni(111)</td>
<td>Previous studies</td>
<td>1.35(^e), 1.47(^d), 1.55(^d), 1.40(^d)</td>
<td>1.18(^d), 1.35(^d), 1.19(^d), 1.15(^d)</td>
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<td>0.80(^b)</td>
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### R7: CHO + O ⇌ HCOO[^1]**

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### R8: HCOO ⇌ CO₂ + H

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### R9: H + H ⇌ H₂

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<td>0.97[^9]**</td>
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[^1]: The activation and reaction energies are ZPVE-corrected values.  
[^2]: Reference [58] (GGA-RPBE calculations using a 2×2 unit cell and three layer slab).  
[^3]: Reference [76] (GGA-RPBE calculations using a 2×2 unit cell and four layer slab).  
[^4]: Reference [52] (GGA-PW91 calculations using a 2×2 unit cell and four layer slab).  
[^5]: Reference [12] (GGA-PW91 calculations using a 2×2 unit cell and four layer slab).  
[^6]: Reference [26] (GGA-RPBE calculations using a 2×2 unit cell and three layer slab).  
[^7]: Reference [15] (GGA-PW91 calculations using a 4×4 unit cell and five layer slab).  
[^8]: Reference [91] (GGA-PBE calculations using a 2×2 unit cell and three layer slab).  
[^9]: Reference [20] (GGA-PBE calculations using a 3×2 unit cell and three-four layer slab).  
[^10]: This is the value without ZPVE corrections.

The WGS reaction starts by H₂O splitting to OH and H since adsorbed carbon monoxide cannot react directly with H₂O [15, 28]. The activation barrier of both water and OH splitting reactions decreases in the order Ni(100) > Ni(111) > Ni(110). The water splitting barriers are far larger than the adsorption energies for water on both the Ni(111) and Ni(100) surfaces. Therefore, even when considering the effect of dispersion forces (which are neglected in the present calculations) it is expected that most of the water molecules desorb without proceeding to OH + H species. This is consistent with experimental observations where heating a Ni(111) surface to 165 K leads to desorption of a water monolayer without formation of water splitting products [107, 108]. In contrast, the calculated binding energy is slightly higher than the splitting barrier on the Ni(110) surface. This is in agreement with experimental studies where the splitting product, OH, is observed at temperatures larger than 200 K [107]. The calculated barrier of water splitting (0.38 eV) is similar to the experimental value of 0.5 eV reported by Benndorf et al. [109] for HO-H bond breakage on the clean Ni(110) surface.

Carbon monoxide can react with the water splitting products (OH, O and H) via the direct, carboxyl and formate pathways.

In the direct (or redox) pathway (see Figure 3(a)) the CO species interacts with O to form CO₂. This step is also considered as the key elementary step in the CO oxidation reaction [110-113]. The activation energies obtained for this step are 1.35 eV, 1.25 eV and 1.57 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The reaction is endothermic on all surfaces. The results suggest that oxidation of CO is faster on the Ni(111) and Ni(100) surfaces compared to the Ni(110) surface.
Figure 3. Reaction profiles for the WGS reaction on Ni(111) (solid black line), Ni(100) (long-dashed blue line) and Ni(110) (short-dashed line) via (a) direct, (b) carboxyl and (c) formate pathways. The zero energy reference is adsorbed water on the nickel surfaces.

In the carboxyl pathway (see Figure 3(b)), adsorbed carbon monoxide reacts with the OH species to form COOH that is bonded to the surface via its carbon atom. The calculated activation energies for this step are 1.30 eV, 1.73 eV and 1.44 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The carboxyl intermediate subsequently dissociates to carbon dioxide and hydrogen with activation energies of 0.68 eV, 1.21 eV and 1.07 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. Both reactions are endothermic on all surfaces except COOH dissociation on the Ni(111) and the Ni(110) surfaces, which is slightly exothermic with an energy of −0.02 eV and −0.16 eV, respectively.

In the formate pathway (see Figure 3(c)) the adsorbed carbon monoxide endothermically reacts with an adsorbed hydrogen atom to produce formyl. The activation energies are 1.53 eV, 1.36 eV and 1.29 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The trends presented here are the same as those reported in experimental studies, i.e., the activation energy obtained on
the Ni(111) surface is higher than that for the Ni(100) surface. The experimental values reported for CO hydrogenation on the Ni(111) and Ni(100) surfaces are 1.67 eV [114] and 1.07 eV [7], respectively. CHO subsequently oxidizes to formate (HCOO) with activation energies of 0.67 eV, 1.47 eV and 0.99 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The reaction is exothermic on all surfaces. The formate then dissociates to CO$_2$ and H. This step is endothermic on all surfaces with an activation barrier of 2.74 eV, 2.76 eV and 1.07 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The endothermic formyl formation and its exothermic oxidation indicate that CHO is an unstable intermediate unlike HCOO, which has a high barrier for dissociation. This could be the reason that formate is the intermediate that is most frequently observed in WGS experiments [115-120].

The remaining elementary step of the WGS reaction is the formation of H$_2$ from the adsorbed H atoms (with subsequent desorption of the H$_2$ molecule). This step is endothermic on all surfaces and the calculated activation energies are 0.81 eV, 0.88 eV and 0.42 eV on the Ni(111), Ni(100) and Ni(110) surfaces, respectively. The calculated activation energies are slightly smaller than the reaction energies on Ni(111) and Ni(100) surfaces. However, this is within the statistical uncertainty of the method since DFT-GGA accuracy is about 0.1 eV [121]. The similarity of these energies indicates that the transition states are very late. This is in agreement with the data in Table S9 where it can be seen that the distances between the hydrogen atoms, which were initially more than 2.5 Å apart (2.5, 3.5 and 4.3 Å for the Ni(111), Ni(100) and Ni(110) surfaces, respectively) decrease to be within about 0.2 Å of the product H-H bond lengths. The similarity of $E_a$ and $\Delta E$ has also been seen previously. Lin et al. [15] and Catapan et al. [12] found a difference of 0.03 eV and 0.08 eV between $E_a$ and $\Delta E$ on the Ni(111) surface, respectively.

All of the imaginary vibrational frequencies obtained for the transition states are in good agreement with previously reported data, except for the water dissociation on the Ni(100) surface. Seenivasan et al. [76] reported a higher vibrational frequency compared to that obtained here. The reason for the discrepancy is not known.

The d-band centre describes the distribution of surface electronic energy levels [66, 122] and the ability to share electron density from the d-band of the metal to the adsorbate. This can explain differences in catalytic activity of the different surfaces, and it is believed that the surface is more reactive when the d-band centre is closer to the Fermi level [66, 122]. The calculated d-band centres are at −1.75, −1.98 and −2.08 eV for the Ni(110), Ni(100) and Ni(111) surfaces, respectively [72]. Therefore, the Ni(110) surface is expected to be the most reactive surface. This is the case for reactions R1, R2, R6, R8 and R9. However, for reactions R4, R5 and R7 the lowest barrier is obtained on the Ni(111) surface, and for R3 the lowest barrier is obtained on the Ni(100) surface.

It may be noted that, for any given metal, the adsorption energy of an atom is, in general, significantly dependent on the adsorption site [123]. Therefore the intensity of the occupied orbitals or the d-band center may be used to predict trends in the adsorption energy or the structure sensitivity if the adsorption site is identical on the metal surface.

3.4. Transition state scaling
The transition state scaling (TSS) method [124, 125], which is often used interchangeably with the Brønsted-Evans-Polanyi (BEP) [126, 127] relationship, correlates the energy of the transition state (ETS) with the energy of either the initial state (EIS) or final state (EFS) of a reaction. TSS and BEP correlations have been reported for reactions similar to those studied here on both flat and stepped metal surfaces [12, 15, 128]. The results obtained here support the validity of the TSS method. Figure 4 shows the correlation between E_{TS} and E_{FS} for all of the forward elementary steps on all Ni surface structures studied here. The data yield a R^2 value of 0.99. This linear scaling relation offers the possibility of estimating the activation barrier for any relevant elementary step occurring on these Ni surfaces based only on the final state energies, E_{FS}. This would avoid time consuming CI-NEB calculations. Also, since the CI-NEB calculations can be avoided, more elementary reactions could be studied to develop a complete kinetic model of any reaction based on accurate DFT results.

It should be noted that only three Ni facets have been studied in this work, and studies of more facets would improve the statistical relevance of the results.

3.5. Comparison of the different reaction pathways

Figure 5 shows the energy profiles for the direct, carboxyl and formate pathways of CO oxidation to CO2 on the Ni(111), Ni(100) and Ni(110) surfaces.
Figure 5. Reaction profiles for the WGS reaction on (a) Ni(111), (b) Ni(100) and (c) Ni(110) via direct (long-dashed purple line), carboxyl (short dashed green line) and formate pathways (solid orange line). The solid black line represents the water dissociation reactions (R1 and R2). The zero energy reference is adsorbed water on the nickel surfaces.

The direct and the carboxyl pathways are preferred on the Ni(111) surface due to the lower barriers for consuming CO. Carbon dioxide is produced directly from CO via the direct pathway (R3), where the activation energy is 1.35 eV. There is a 1.30 eV barrier for producing COOH from CO and OH via the carboxyl pathway (R4), and this intermediate can then dissociate to CO$_2$ and H (R5) with a barrier of 0.68 eV. However, the barrier for the reverse reaction of R4 is almost half of the R5 reaction barrier, i.e. 0.31 eV compared to 0.68 eV. Hence, compared to the direct pathway, the rate of formation of CO$_2$ is lowered by the two activation barriers (R4 and R5) and the fact that the reverse of R4 (COOH $\rightarrow$ CO and OH) is faster than R5 (formation of CO$_2$).

The barrier for CO hydrogenation (R6), which is part of the formate pathway, is about 0.2 eV higher compared to its oxidation (R3 in the direct pathway). In addition, the dissociation barrier of the produced CHO (via the reverse of reaction R6) is considerably lower than the activation
barrier of R7 (formate production). Also, the barrier of formate dissociation to CO₂ and hydrogen is very large (2.74 eV) which makes reaction via the formate pathway very slow. Therefore, direct and carboxyl pathways are preferred and, since they have similar activation energies, are competing mechanisms. However, as described above, the direct pathway is favored and reaction R3 (CO + O → CO₂) is the rate determining step on the Ni(111) surface.

The direct pathway is also preferred on the Ni(100) surface since the reaction barrier for carbon monoxide consumption in this pathway (R3: 1.25 eV) is smaller than in the formate pathway (R6: 1.36 eV) and in the carboxyl pathway (R4: 1.73 eV). The formyl produced via R6 is oxidized to HCOO (R7) which is a stable intermediate due to its high barrier for CO₂ production (R8: 2.76 eV) and the large barrier for its dissociation to formyl and oxygen (reverse of R7, 1.47 eV). In addition, formyl can dissociate to CO and H (reverse of R6) instead of oxidizing to CO₂ (R7), since the barrier of the dissociation (reverse of R6) is almost one third of the barrier for its oxidation (R7), i.e., 0.48 compared to 1.47 eV. Consequently, similarly to the Ni(111) surface, the direct pathway is the main route of the WGS reaction on the Ni(100) surface, and the rate limiting step is the oxidation of carbon dioxide, i.e., reaction R3.

A similar analysis for the Ni(110) surface shows that the hydrogenation of CO (R6), which occurs in the formate pathway, has a lower barrier (1.29 eV) than CO oxidation (R3, direct pathway, 1.57 eV) or CO reacting with OH (R4, carboxyl pathway, 1.44 eV). However, the CHO which is formed via reaction R6 has a large barrier (0.99 eV) to form formate via reaction R7. In addition, the barrier of the reverse of R6 (0.16 eV) is very low compared to R7 (0.99 eV) which further hinders the formation of formate via R7. This indicates that the formate pathway is not the main pathway for CO₂ production.

A similar argument holds when comparing the direct and carboxyl pathways. The reaction involving CO via the carboxyl intermediate (R4) to form COOH has a barrier of 1.44 eV. An additional barrier of 1.07 eV needs to be surmounted for the COOH to form CO₂. Also, the barrier for the reverse of R4 is far smaller than the barrier of R5, i.e., 0.26 eV compared to 1.07 eV. This further reduces the rate of CO₂ production via the carboxyl pathway. Therefore, CO₂ is primarily produced via the direct pathway, similarly to the other two surfaces, and R3 is the rate determining step.

Hence, the direct pathway is preferred on all three Ni surfaces. Also, the activation energies for this pathway decrease in the order Ni(110) (1.57 eV) > Ni(111) (1.35 eV) > Ni(100) (1.25 eV). Therefore, if O intermediates are present on the Ni surface the direct pathway on the Ni(100) will be the dominant mechanism. However, as discussed above, the barriers for H₂O dissociation are larger than for H₂O desorption on the Ni(111) and Ni(100) surfaces. Hence, at low H₂O(g) pressures the direct pathway on the Ni(110) will dominate.

It may be noted that ideal nickel surfaces are investigated in the present study for the reasons given in Section 2.2. However, since the oxidation of CO (R3) is the rate limiting step, a buildup of oxygen atoms on the surface is expected which may lead to surface reconstruction. This needs to be studied in future work.

It also may be noted that it is difficult to determine the dominant pathway or the rate determining step based only on the DFT-calculated energetics since several pathways have been studied for the WGS reaction on these Ni surfaces. Therefore a kinetics analysis, which is about rates and not
only activation energies, is necessary to investigate such a complex reaction network and to find out which steps are irrelevant from a kinetics point of view. This also remains as future work.

The results obtained from the DFT calculations are consistent with those previously reported for the WGS reaction on nickel and other metal surfaces [10, 123, 129-133]. For example, Li et al. [131] measured steady state WGS kinetics from 250 to 300°C for a Ni-loaded cerium oxide catalyst. They found that the Ni-Ce(La)Ox catalyst is superior to the support itself, i.e., Ce(La)Ox. They proposed a direct reaction mechanism involving oxidation of adsorbed carbon monoxide by oxygen supplied to the metal interface by ceria. Hilaire et al. [133] studied the WGS reaction over ceria supported metallic catalysts including nickel. Their study showed that the mechanism for the reaction involves a direct pathway. Wang et al. [123] used DFT calculations to investigate the forward and reverse WGS reaction on Cu(111), Cu(100), and Cu(110) surfaces assuming the direct pathway. They also found that these reactions are sensitive to the surface structure and concluded that the difference in adsorption energy of atomic oxygen or other strongly adsorbed species in their transition state structure is important to account for the structure-sensitive reactions. Nakamura et al. [132] used LEED to investigate the kinetics and mechanisms of the WGS reaction on Cu(110) and Cu(111) surfaces. They suggested that adsorbed OH produces atomic oxygen which then reacts with CO to produce carbon dioxide via the direct mechanism. In contrast, based on their DFT results, Catapan et al. [12] suggested the carboxyl pathway as the favored route on the Ni(111) surface, since they found the lowest barrier for consuming CO is via this route. However, it is important to note that this result (the lowest barrier being in the carboxyl pathway) is also found in the present work. The difference is due to the interpretation of the results. In the present study, the reverse reaction (reverse of R4) was taken into the account which slows down the reaction via the carboxyl pathway, since it has a lower barrier compared to R5.

It can also be noted that formate is a stable intermediate on all surfaces due to its high dissociation barriers. There are two routes for formate dissociation. One is HCOO dissociation to CHO and O (reverse of R7) and the other one is dissociation to CO2 and H (R8). The barriers for both of these reactions are higher than 1 eV. The stability of HCOO on metal surfaces and its consequent role in WGS reaction is well known [18-20, 129, 130]. For instance, based on a microkinetic model of the low-temperature WGS reaction over Cu-based catalysts, Ovesen et al. [129] suggested that formate may be present on the surface, but it is a “dead end” in the WGS reaction and it is not a participating species in the conversion of CO to CO2. They suggest that its main effect is to block the active sites. This is consistent with the results reported here. Also, several spectroscopy studies report the presence of formate on Ni surfaces [17-21, 134].

In addition to the energetics, the main pathway of carbon dioxide formation is dependent on the coverage of the co-reactant, O, which favors the direct path, OH, which favors the carboxyl path, or H, which favors the formate path. Phatak et al. [135] investigated the O and OH coverage on metallic surfaces and found that OH dominates on Pt, Pd, Cu and Au, whereas both OH and O are dominant on Ni under low temperatures and high H2 partial pressures. This supports the suggestion that the energetics may be a proper indicator of the dominant pathway of the WGS reaction on Ni.
4. Conclusions

The effect of three different nickel surface structures on the mechanism and rate of the WGS reaction has been studied using DFT. The same models and methods were used for all surfaces to enable comparison of the effect of the surface on the reaction and activation energies. The adsorption energy for ten surface species involved in the WGS reaction were calculated together with activation barriers and reaction energies for the nine most important elementary steps.

The results indicate that the Ni(110) surface has the lowest barrier for water dissociation (reactions R1 and R2), formyl formation (R6), formate dissociation (R8) and H₂ formation (R9), and that the lowest barrier for CO oxidation to CO₂ (R3) is on the Ni(100) surface. Also, H₂O, OH, HCOO, CO₂ and H₂ bind strongest to the Ni(110) surface while COOH, CHO, CO, O and H bind strongest to the Ni(100) surface. The co-adsorbed structures were also investigated. In all cases the co-adsorption sites are the same as those found for the individual adsorbates except for oxygen on the Ni(110) surface.

Analysis of energetics shows that the direct pathway is favored on all three surfaces via the reaction CO + O → CO₂, which is therefore the rate limiting step. The barrier obtained for this elementary reaction decreases in the order Ni(110) > Ni(111) > Ni(100). Therefore, based on DFT calculations, if adsorbed oxygen atoms are present the Ni(100) surface is more active for the WGS reaction compared to the other surfaces. However, since the barriers for H₂O dissociation are larger than for H₂O desorption on the Ni(111) and Ni(100) surfaces, but not the Ni(110) surface, the direct pathway on the Ni(110) will dominate at low H₂O(g) pressures.

BEP relationships are valid for these reactions on these surfaces, with an R² value of 0.99.

The results also indicate that formate is a stable intermediate on all surfaces because of its high dissociation barriers. This could be the reason for the experimental observations of formate on Ni surfaces. Thus formate is not an active species in the conversion of CO to CO₂ in the WGS reaction. The results presented here agree with data from previous studies when available.

Acknowledgments

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DFT study of water gas shift reaction on Ni(111), Ni(100) and Ni(110) surfaces

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Table S1. Adsorption energies (eV) and structural parameters (Å and degrees) of the chemical species involved in the \( \text{H}_2\text{O} \Leftrightarrow \text{OH} + \text{H} \) elementary reaction. The adsorption energies are ZPVE-corrected values. \( d_{\text{surf-O}} \) and \( d_{\text{surf-H}} \) are the shortest distances between oxygen and hydrogen atoms of the adsorbate and any metal atom on the surface. \( d_{\text{O-H}} \) is the bond distance between O and H. The bond which is broken during the reaction is marked by \( (b) \).

<table>
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<th>Species</th>
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<th>( E_{\text{ads}} )</th>
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<th>( d_{\text{surf-H}} )</th>
<th>( d_{\text{O-H}} )</th>
<th>( \theta_{\text{H-O-H}} )</th>
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<td>1.538(b)</td>
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Table S2. Adsorption energies (eV) and structural parameters (Å) of the chemical species involved in the \( \text{OH} \Leftrightarrow \text{O} + \text{H} \) elementary reaction. The adsorption energies are ZPVE-corrected values. \( d_{\text{surf-O}} \) and \( d_{\text{surf-H}} \) are the shortest distances between oxygen and hydrogen atoms of the adsorbate and any metal atom on the surface. \( d_{\text{O-H}} \) is the bond distance between O and H.

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<th>( d_{\text{O-H}} )</th>
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Table S3. Adsorption energies (eV) and structural parameters (Å and degrees) of the chemical species involved in the \( \text{CO} + \text{O} \rightleftharpoons \text{CO}_2 \) elementary reaction. The adsorption energies are ZPVE-corrected values. \( d_{\text{surf-C}} \) and \( d_{\text{surf-O}} \) are the shortest distances between carbon and oxygen atoms of the two different adsorbates and any metal atom on the surface. \( d_{\text{C-O}} \) is the bond distance between C and O. The bond which is broken during the (reverse) reaction is marked by (b).

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface</th>
<th>Site</th>
<th>( E_{\text{ads}} )</th>
<th>( d_{\text{surf-C}} )</th>
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<th>( d_{\text{C-O}} )</th>
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Table S4. Adsorption energies (eV) and structural parameters (Å and degree) of the chemical species involved in the \( \text{CO} + \text{OH} \rightleftharpoons \text{COOH} \) elementary reaction. The adsorption energies are ZPVE-corrected values. \( d_{\text{surf-C}} \) and \( d_{\text{surf-O}} \) are the shortest distances between carbon and oxygen atoms of the two different adsorbates and any metal atom on the surface. \( d_{\text{C-O}} \) and \( d_{\text{O-H}} \) is the bond distance between C and O, and O and H. The bond which is broken during the (reverse) reaction is marked by (b).

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Table S5. Adsorption energies (eV) and structural parameters (Å) of the chemical species involved in the COOH ⇌ CO2 + H elementary reaction. The adsorption energies are ZPVE-corrected values. $d_{\text{surf-C}}$ and $d_{\text{surf-H}}$ are the shortest distances between carbon and hydrogen atoms of the two different adsorbates and any metal atom on the surface. $d_{\text{C-O}}$ and $d_{\text{O-H}}$ is the bond distance between C and O, and O and H.

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<th>$d_{\text{surf-C}}$</th>
<th>$d_{\text{surf-H}}$</th>
<th>$d_{\text{C-O}}$</th>
<th>$d_{\text{O-H}}$</th>
<th>$\theta_{\text{O-C-O}}$</th>
<th>$\theta_{\text{H-C-O}}$</th>
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<td>Ni(111)</td>
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<td>−2.17</td>
<td>1.858</td>
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<td>C-O: 1.270</td>
<td>0.988</td>
<td>117.9</td>
<td>107.5</td>
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<td>C:B</td>
<td>−2.70</td>
<td>1.961</td>
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<td>C: E</td>
<td>−2.55</td>
<td>1.873</td>
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<td>C-O: 1.266</td>
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<td>138.3</td>
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Table S6. Adsorption energies (eV) and structural parameters (Å and degree) of the chemical species involved in the CO + H ⇌ CHO elementary reaction. The adsorption energies are ZPVE-corrected values. $d_{\text{surf-C}}$ and $d_{\text{surf-H}}$ are the shortest distances between carbon and hydrogen atoms of the two different adsorbates and any metal atom on the surface. $d_{\text{C-O}}$ and $d_{\text{C-H}}$ are the bond distance between C and O, and C and H.

| Species | Surface | Site | $E_{\text{ads}}$ | $d_{\text{surf-C}}$ | $d_{\text{surf-H}}$ | $d_{\text{C-O}}$ | $d_{\text{C-H}}$ | $\theta_{\text{H-C-O}}$ |
|---------|---------|-----|-----------------|-------------------|-------------------|-----------------|----------------|---------------------|---------------------|
| CO + H  | Ni(111) | C: C | −4.54          | 1.947             | 1.694             | 1.191           | ---             | ---                 |
|         | Ni(100) | C: D' | −4.61         | 2.037             | 1.833             | 1.213           | ---             | ---                 |
|         | Ni(110) | C: F | −4.51          | 1.874             | 1.691             | 1.181           | ---             | ---                 |
| TS      | Ni(111) | C: A | ---            | 1.942             | 1.938             | 1.261           | 1.155           | 118.6               |
|         | Ni(100) | C: B | ---            | 1.875             | 1.605             | 1.244           | 1.306           | 114.8               |
|         | Ni(110) | C: F | ---            | 1.796             | 1.942             | 1.234           | 1.159           | 122.5               |
| CHO     | Ni(111) | C: B | −2.19          | 1.960             | ---               | 1.289           | 1.110           | 117.0               |
|         | Ni(100) | C: B | −2.76          | 1.916             | ---               | 1.353           | 1.111           | 112.5               |
|         | Ni(110) | C: F | −2.42          | 1.807             | ---               | 1.257           | 1.116           | 117.9               |
Table S7. Adsorption energies (eV) and structural parameters (Å and degree) of the chemical species involved in the CHO + O ⇌ HCOO elementary reaction. The adsorption energies are ZPVE-corrected values. $d_{surf-C}$ and $d_{surf-O}$ are the shortest distances between carbon and oxygen atoms of the two different adsorbates and any metal atom on the surface. $d_{C-O}$ and $d_{C-H}$ is the bond distance between C and O, and C and H. The bond which is broken during the reaction is marked by (b).

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<th>$d_{C-O}$</th>
<th>$d_{C-H}$</th>
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<td>C-O: 1.272</td>
<td>1.109</td>
<td>O$_1$-C-H: 115.1</td>
</tr>
<tr>
<td></td>
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<td>O$_2$: A</td>
<td></td>
<td></td>
<td>O$_2$: 1.921(b)</td>
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</table>


Table S8. Adsorption energies (eV) and structural parameters (Å and degree) of the chemical species involved in the HCOO ⇌ CO₂ + H elementary reaction. The adsorption energies are ZPVE-corrected values. \(d_{\text{surf-C}}\), \(d_{\text{surf-O}}\) and \(d_{\text{surf-H}}\) are the shortest distances between carbon, oxygen and hydrogen atoms of the adsorbate and any metal atom on the surface. \(d_{\text{C-O}}\) and \(d_{\text{C-H}}\) is the bond distance between C and O, and C and H.

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface</th>
<th>Site</th>
<th>(E_{\text{ads}})</th>
<th>(d_{\text{surf-C}})</th>
<th>(d_{\text{surf-O}})</th>
<th>(d_{\text{surf-H}})</th>
<th>(d_{\text{C-O}})</th>
<th>(d_{\text{C-H}})</th>
<th>(\theta)</th>
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<td>O₂: 1.961</td>
<td>O₂: 1.963</td>
<td>---</td>
<td>C₂: 1.272</td>
<td>O₂: 1.271</td>
</tr>
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<td>O₂: A</td>
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<td>O₂: 1.963</td>
<td>---</td>
<td>C₂: 1.294</td>
<td>O₂: 1.259</td>
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<td>O₃-C-H: 115.8</td>
</tr>
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<td>O₂: A</td>
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<td>O₃-C-H: 115.1</td>
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Table S9. Adsorption energies (eV) and structural parameters (Å) of the chemical species involved in the \(\text{H}_2 \rightleftharpoons \text{H} + \text{H}\) elementary reaction. The adsorption energies are ZPVE-corrected values. \(d_{\text{surf-H}}\) is the shortest distances between hydrogen atoms any metal atom on the surface. \(d_{\text{H-H}}\) is the bond distance between hydrogen atoms.

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface</th>
<th>Site</th>
<th>(E_{\text{ads}})</th>
<th>(d_{\text{surf-H}})</th>
<th>(d_{\text{H-H}})</th>
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Table S10. Adsorption energies (eV) and structural parameters (Å) of CO, O and H. The adsorption energies are ZPVE-corrected values. $d_{\text{surf-adsorbate}}$ is the shortest distance between carbon, oxygen and hydrogen atoms and any metal atom on the surface. $d_{\text{C-O}}$ is the bond distance between C and O.

<table>
<thead>
<tr>
<th>Species</th>
<th>Surface</th>
<th>Site</th>
<th>$E_{\text{ads}}$</th>
<th>$d_{\text{surf-adsorbate}}$</th>
<th>$d_{\text{C-O}}$</th>
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<tbody>
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<td>Ni(110)</td>
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<td>1.700</td>
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</table>
Figure S1. Reactant, transition state and product structures for the H₂O ⇌ OH + H reaction.

Figure S2. Reactant, transition state and product structures for the OH ⇌ O + H reaction.

Figure S3. Reactant, transition state and product structures for the CO + O ⇌ CO² reaction.
Figure S4. Reactant, transition state and product structures for the CO + OH ⇌ COOH reaction.

Figure S5. Reactant, transition state and product structures for the COOH ⇌ CO₂ + H reaction.

Figure S6. Reactant, transition state and product structures for the CO + H ⇌ CHO reaction.
Figure S7. Reactant, transition state and product structures for the CHO + O ⇌ HCOO reaction.

Figure S8. Reactant, transition state and product structures for the HCOO ⇌ CO₂ + H reaction.

Figure S9. Reactant, transition state and product structures for the H + H ⇌ H₂ reaction.