FIRST PRINCIPLES INVESTIGATION OF HETEROGENEOUS CATALYSIS ON METAL OXIDE SURFACES

by

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A thesis submitted in conformity with the requirements for the degree of Masters of Applied Science
Graduate Department of Materials Science and Engineering
University of Toronto

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Abstract

First Principles Investigation of Heterogeneous Catalysis on Metal Oxide Surfaces

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Metal oxides possess unique electronic and structural properties that render them highly favourable for applications in heterogeneous catalysis. In this study, computational atomistic modelling based on Density Functional Theory was used to investigate the reduction of carbon dioxide over hydroxylated indium oxide nanoparticles, as well as the activation of methane over oxygen-covered bimetallic surfaces. The first study employed metadynamics-biased ab initio molecular dynamics to obtain the free energy surface of the various reaction steps at finite temperature. In the second study, the nudged elastic band method was used to probe the C-H activation mechanisms for different surface configurations. In both cases, activation energies, reaction energies, transition state structures, and charge analysis results are used to explain the underlying mechanistic pathways.
To Michelle.
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<td>AIMD</td>
<td>Ab Initio Molecular Dynamics</td>
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<tr>
<td>BO</td>
<td>Born-Oppenheimer</td>
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<tr>
<td>CI-NEB</td>
<td>Climbing-Image Nudged Elastic Band</td>
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<tr>
<td>CV</td>
<td>Collective Variable</td>
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<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
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<tr>
<td>FCC</td>
<td>Face Centered Cubic</td>
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<tr>
<td>FES</td>
<td>Free Energy Surface</td>
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<tr>
<td>FLP</td>
<td>Frustrated Lewis Pair</td>
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<tr>
<td>GGA</td>
<td>Generalized Gradient Approximation</td>
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<tr>
<td>HCP</td>
<td>Hexagonal Close Packed</td>
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<tr>
<td>LDA</td>
<td>Local-density approximation</td>
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<td>MD</td>
<td>Molecular Dynamics</td>
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<td>MetaD</td>
<td>Metadynamics</td>
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<td>NEB</td>
<td>Nudged Elastic Band</td>
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<td>PBE</td>
<td>Perdew-Burke-Ernzerhof</td>
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<tr>
<td>RRKJ</td>
<td>Rappe-Rabe-Kaxiras-Joannopoulos</td>
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<tr>
<td>RWGS</td>
<td>Reverse Water Gas Shift</td>
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<td>SMR</td>
<td>Steam Methane Reforming</td>
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<td>TS</td>
<td>Transition state</td>
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Chapter 1

Introduction

1.1 Background Information

Metal oxides hold tremendous importance for heterogeneous catalysis. Their unique structural, electronic, and optical properties enable them to be used in a variety of catalytic processes. Indeed, the majority of today’s commercial catalysts consist of an amalgamation of metal particles integrated onto a metal oxide support. [1] The catalytic properties of metal oxides are largely influenced by the presence of structural and chemical defects which, in turn, affect the stability and reactivity of the surface. Still, despite many research efforts, there remains no general theory to explain how such defects influence the material’s capacity to be catalytic. [1, 2]

Anthropogenic carbon dioxide emissions have been consistently rising since the time of the Industrial Revolution and the amount of carbon dioxide currently present in the Earth’s atmosphere is more than 1.4 times pre-industrial concentrations (Figure 1.2). This, in conjunction with rapid population growth and increasing demands for elevated standards of living, has created an urgency to find a way of meeting global energy demands in a sustainable manner. The greatest source of greenhouse gas emissions is currently the production of energy and more that 80% of the energy used today is derived from fossil fuel sources [3], the principle culprit driving climate change. It has become imperative that the global energy economy shifts towards sustainable, carbon-neutral fuel sources in order keep the global rise in temperature well below the recently proposed 2 °C limit. [3] Catalyst materials inherently improve the efficiency of reactions, and offer substantial reductions in emissions to many industrial processes, such as chemical synthesis, electronics manufacturing, as well as energy production. [2] Unlocking their catalytic potential will be the key driving sustainable energy innovation.

Metal oxides have been demonstrated as promising catalyst materials for both aque-
ous and gas-phase catalysis. [4, 5, 6, 7, 8]. TiO$_2$ has been found to be the most stable metal oxide for photocatalytic conversion of H$_2$O and CO$_2$ [6, 8], Cu/ZnO$_2$ has been demonstrated to reduce CO$_2$ to methanol via a hydrogenation reaction [9], Ag$_2$O has been shown to electrocatalytically convert CO$_2$ to CO [8], and In$_2$O$_3$ is capable of heterogeneous photocatalytic reduction of CO$_2$ to CO [10]. While much of the research in metal oxide catalysis has focused on homogeneous aqueous-phase catalysis, the focus of the present work is gas-phase. Liquid-liquid and liquid-gas interfaces may demonstrate high catalytic rates; however, such systems require an initial costly energy input to sequester the gas-phase reagents, as is the case for the catalytic reduction of CO$_2$. A cheap, abundant, and robust metal oxide capable of gas-phase photochemical or thermochemical catalysis would therefore be the ideal solution for efficient industrial-scale implementation. Computational modelling based on first-principles is a particularly useful approach to investigate reactions that ensue on catalyst surfaces. The work here presented is comprised of two Density Functional Theory (DFT) studies that involve heterogeneous gas-phase catalysis over metal oxide surfaces. The first is a finite-temperature DFT-based study on the reduction of CO$_2$ over hydroxylated indium oxide nanoparticles. The second is a ground-state DFT study of methane reduction over oxygenated Ni-based bimetallic catalyst systems. The background into each of these investigations is described in greater detail below.

Figure 1.1: Energy transitions since the year 1900: it takes decades to develop and adopt new sources of energy. [3]
Figure 1.2: Keeling curve showing the increase in CO₂ concentration since the Industrial Revolution. [11]

1.1.1 Reducing CO₂ to Create Solar Fuels

The conversion of greenhouse gas CO₂, emitted from energy exhaust streams, into fuels and chemical feedstocks, such as methane, methanol, and carbon monoxide, offers a promising path to building a carbon neutral economy (see Figure 1.3). [12]

Figure 1.3: Schematic depicting an energy economy based on solar fuels production.[12]

The production of such sustainable fuels, termed “solar fuels”, has led to a widespread
investigation by the scientific community to find a cheap and abundant photo- or thermocatalyst material capable of efficiently splitting gaseous CO$_2$. [12] The photocatalytic reduction of CO$_2$ presents a set of challenges, as few gas-phase photocatalysts operate in the visible light spectrum. [10] The presence of oxygen vacancies in metal oxide systems, such as black titania and indium oxide, have been shown to simultaneously serve as active surface sites and widen the material’s absorption spectra. [6, 10, 13] Other surface defects, such as the introduction of surface hydroxides, have also been shown to facilitate the capture of adsorbate molecules. [7, 10, 14] Indium oxide (In$_2$O$_3$) is a particularly favourable choice for the photocatalytic reduction of CO$_2$, as its electronic band structure aligns with the potentials of the H$_2$O oxidation and CO$_2$ reduction half reactions, enabling it to potentially produce hydrocarbons and carbon monoxide simultaneously. [15]. As well, its electronic structure contains forbidden band regions that may impede electron-hole pair recombination and prolong charge carrier lifetime. [10] Hydroxylated indium oxide (In$_2$O$_{3-x}$(OH)$_y$) nanoparticles have been demonstrated to assist in the Reverse Water Gas Shift (RWGS) reaction (CO$_2$ + H$_2$ $\rightarrow$ CO + H$_2$O) by heterolytically splitting H$_2$ and subsequently reducing CO$_2$. [10, 14] The thermal-sensitvity of the reaction requires an understanding of the fundamental interplay between the active surface sites and temperature, and its consequences for the RWGS reaction mechanism.

1.1.2 Catalysts for Improving Steam Methane Reforming

The steam methane reforming (SMR) reaction, in which methane is reduced to produce hydrogen and carbon monoxide (CH$_4$ + H$_2$O $\rightarrow$ CO + H$_2$), is currently the largest industrial producer of commercial hydrogen. [16] While the shift towards hydrogen as an energy carrier could potentially address the aforementioned issues in sustainable energy production, the SMR industry is mostly restricted to using natural gas as a hydrocarbon source, and predominantly serves as the precursor to the Fischer-Tropsch process, which consists of the conversion of carbon monoxide and hydrogen (ie. syngas) into liquid hydrocarbons. As it currently sits in this energy chain, SMR is not a sustainable way of producing hydrogen. [17] Still, many established industrial processes, such as the production of ammonia, currently rely on SMR, and while we still require a breakthrough in hydrogen-producing technologies that are not based on fossil-fuels, SMR could sustain the initial move into the hydrogen fuel economy. [17, 16] Alternatively, reactions of biomass-derived methane with carbon dioxide could offer a more sustainable route for the production of carbon monoxide and hydrogen mixtures as precursors for synthesizing commodity chemicals and liquid fuels (Figure 1.4). [16]
Methane, being both the most abundant and most hydrogen-rich hydrocarbon, serves as a prime source of H\textsubscript{2}. A recent report from the Canadian Gas Association has estimated a potential of producing 24.9 Mt/yr of methane as renewable gas from Canadian waste, while in the US, it is estimated that wastewater, landfills, animal manure, and organic waste sources have the potential to generate up to 7.8 Mt/year of renewable methane gas. In 2013 alone, there were 11.34 trillion cubic feet of shale gas produced in the US. The emerging economy in shale gas is driving the demand for new catalytic technology that can transform methane into synthesis gas for remote conversion of the stranded gas into valuable, liquid fuels or chemicals. However, the technology to process methane derived from natural gas and biogas is currently lacking. The challenge is to develop catalyst materials that are extremely robust, reliable, and can be used continuously under industrial conditions. In particular, the catalyst must be resistant to coke deposition and sulfur poisoning. Multiple studies have established the detailed pathways of methane activation catalyzed by transition metal clusters. The introduction of a secondary transition metal (TM) to the nickel-based catalyst has proven to reduce the formation of unwanted carbon products in the SMR and has henceforth uncovered a promising path forward into catalyst optimization for hydrogen production. A improved understanding of the interaction mechanism between adsorbate methane and the bimetallic surface could inspire design of more efficient catalysts.
1.2 Thesis Motivation

As previously mentioned, metal oxides are renown for their catalytic properties; however, an understanding their electronic structure is lacking when compared to other material categories. [1] Establishing a relationship between the properties of the atoms and those of the bulk and surface structures would allow for rapid screening and design of catalyst materials. In the past, the asymmetry and large size metal oxide crystal structures rendered them challenging to investigate using computational modelling [1]; however, recent improvements in computer processor speed and investment in supercomputing facilities have allowed for the reaches of computational chemistry and computational science to rapidly expand. [29] Denstiy Functional Theory (DFT), which considers the quantum mechanical description of electrons, is a particularly useful tool for investigating catalytic reactions because it allows for probing of specific atoms and bonds within a system. Such studies are able to probe ligand and geometrical effects that are otherwise not easily isolated in experiments. DFT, used in conjunction with other numerical simulations, can predict the stable phases, as well as electronic, thermal, and optical properties of a system. In particular, atom-specific information, such as bond lengths, coordination numbers, electronegativity, and oxidation states of specific atoms, provide useful insight when studying heterogeneous catalysis.

1.3 Thesis objectives

In order to address the simultaneous increase in greenhouse gas emissions and growing global energy demands, the objective of the present work is to investigate potential metal oxide materials to serve as reliable gas-phase heterogeneous catalysts for energy applications. Given the history of slow energy transitions, industry and government will take decades to shift away from the current fossil fuel-based energy economy to a more sustainable carbon-neutral energy economy. Taking these considerations in account, this present investigation has two primary objectives: firstly, to find a sustainable alternative energy source to fossil fuels by investigating the catalytic reduction of CO$_2$ to produce solar fuels, and secondly, to improve current fuel production methods to support the transition into a sustainable fuel economy by studying methane reforming catalysts. In particular, this work aims to probe and understand the atomic-level interactions that ensue on catalyst surfaces by computationally obtaining the minimum energy pathways, the transition state structures, and the energetic landscapes, so as to learn which electronic and structural properties may enhance reaction rates. The goals specific to each
of the two global objectives are as follow:

1. **Investigating the reduction of CO\textsubscript{2} over In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y}**
   - Understand the role of temperature on the catalytic RWGS reaction over In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} nanocrystals.
   - Investigate alternate reaction mechanisms that may ensue over In\textsubscript{2}O\textsubscript{3-x}(OH)\textsubscript{y} at finite-temperatures.
   - Determine the factors influencing the activation of H\textsubscript{2} via surface Frustrated Lewis Pairs.

2. **Investigating methane reforming over bimetallic catalysts**
   - Understand the effects of cobalt additives in nickel-based catalysts on the C-H bond activation.
   - Investigate the effect of chemisorbed oxygen on the C-H activation mechanism on nickel-cobalt catalysts.
   - Determine the optimal stoichiometric and structural conditions to improve reaction rates for methane reforming reaction over oxygenated nickel-cobalt catalysts.

### 1.4 Thesis organization

The work begins by providing a theoretical overview of the computational methods used in these studies. Chapter 2 first reviews basic DFT theory and then describes the two extended approaches that are used for modelling reactions: the nudged elastic band method and metadynamics-biased ab initio molecular dynamics. Chapter 3 covers the finite-temperature study of CO\textsubscript{2} reduction over hydroxylated indium oxide nanoparticles. The results are presented in order of each step involved in the Reverse Water Gas Shift (RWGS) reaction. A comparison of the reaction energetics at different temperatures is presented, as well as results showing the effect of doping the catalyst with bismuth. Chapter 4 presents the study on the SMR reaction over nickel-based bimetallic catalysts. Adsorption energy studies, minimum energy reaction pathways, transition state structures, and activation barriers for C-H activation over a variety of nickel-cobalt systems are presented. Chapter 5 summarizes the overall contribution of the work, and lays the grounds for future investigations.
Chapter 2

Modelling Reactions

The chemical properties of materials are determined by a combination of ensemble, geometric, and electronic effects, all of which are fundamentally governed by the Schrödinger equation. The work here presented uses DFT to obtain the energy and structural configuration of a system corresponding to its lowest energy state. The relative energies of different systems were then used to determine the most energetically-stable surfaces, as well as the binding energies of chemical adsorbates. The Nudged Elastic Band (NEB) and Climbing Image Nudged Elastic Band (CI-NEB) methods were used to obtain the reaction pathways, transition state structures, and activation barriers for the methane reforming reaction over Ni-based catalysts. Ab initio molecular dynamics (AIMD) was used in conjunction with metadynamics (MetaD) to simulate the evolution of each step of the RWGS reaction at finite-temperature. The Quantum Espresso software with the added PLUMED plug-in suite was used to carry out all MetaD-biased AIMD calculations. The Vienna Ab Initio Simulation Package (VASP) was used for all DFT calculations of Ni-based bimetallic surfaces.

2.1 Density Functional Theory

The quantum mechanical behaviour of a system is fully described by the Schrödinger equation. In particular, the non-relativistic time-independent Schrödinger equation provides a way to compute the stationary wave function of a system, and is given by the eigenvalue equation:

\[ \hat{H} \Psi = E \Psi \]  

(2.1)
where $\hat{H}$ is the Hamiltonian operator, $\Psi$ are the eigenvectors representing the stationary wavefunctions, and $E$ are the eigenvalues corresponding to the system energy. The Hamiltonian acts upon the wavefunction $\Psi$ and the result is proportional to $\Psi$ by a factor of $E$, which describes the energy of $\Psi$. The Hamiltonian is composed of both kinetic and potential energy contributions and may be expressed as:

$$\hat{H} = T_e(r) + T_N(R) + V_{eN}(r, R) + V_{NN}(R) + V_{ee}(r)$$  \hspace{1cm} (2.2)

where $R$ are the spatial coordinates of the nuclei and $r$ are the spatial coordinates of the electrons. The terms represent, starting from the left: the kinetic energy of electrons, the kinetic energy of nuclei, the potential energy of the electron-nuclei interaction, the potential energy of the nuclei-nuclei interaction, and the potential energy of the electron-electron interaction. The multi-dimensional nature of the partial differential equation makes it increasingly complex and intractable to solve theoretically for systems greater than one or two electrons. DFT is a method that offers a computationally-derived solution for the non-relativistic time-independent Schrödinger equation based on the Hohenberg-Kohn theorems.

### 2.1.1 The Born-Oppenheimer Approximation

Attempting to solve Equation 2.1 is inherently difficult due to the presence of terms that are simultaneously dependent on $r$ and $R$. The Born-Oppenheimer (BO) approximation reduces some of this complexity by exploiting the large difference in electronic and nuclear mass to separate the contributions of the nuclei from those of the electrons such that the wavefunction may be expressed as a product of two independent components: $\Psi(r, R) = \psi(r)\chi(R)$. This formulation allows for a solution based on solving two distinct problems: first, solving for the wavefunctions corresponding to the motions of the electrons, assuming the positions of the nuclei to be fixed; and second, solving for the potential energy resulting from the positions of the nuclei. The number of dimensions involved in the original problem is therefore significantly reduced by decoupling the electronic from the nuclear contributions. These resulting multidimensional potential energy functions describe what is called the Born-Oppenheimer potential energy surface.

### 2.1.2 The Hartree-Fock Approximation

While the BO approximation separates the nuclear from the electronic contributions of the wavefunction, the electronic component itself remains too complex to solve, as it is
a function of all the electron coordinates of the system. The Hartree product allows to express this wavefunction as a product of wavefunctions for $N$ individual electrons:

$$\psi = \psi_1(r_1)\psi_2(r_2), \ldots, \psi_N(r_N)$$ (2.3)

where $\psi_i(r_i)$ is the wavefunction of electron $i$. The Hartree-Fock approximation takes an additional step to satisfy the antisymmetry requirements that arise from the Pauli Exclusion Principle by expressing the product in the form of a Slater determinant. This guarantees an anti-symmetric product of non-interacting wavefunctions to describe the electronic wavefunction.

### 2.1.3 The Hohenberg-Kohn Theorems and the Kohn-Sham Equations

Despite the reduction in complexity offered by the BO approximation and the Hartree-Fock approximation, the individual electron wavefunctions remain a computationally challenging problem. Hohenberg and Kohn provided two invaluable theorems proving that the many-body problem may be reduced to a simpler problem of only three spatial coordinates by solving for the electron density in lieu of the electron wavefunctions (where $3N$ dimensions are needed for $N$ electrons). The electron density, $n(r)$, is a spatial quantity that is defined as a function of the individual wavefunctions:

$$n(r) = 2 \sum_i \psi_i^*(r)\psi_i(r)$$ (2.4)

Hohenberg and Kohn’s first theorem states that the ground state energy of a system, as determined by the Schrödinger equation, is a unique functional of the electron density. The second theorem states that the electron density which minimizes the energy functional is the true electron density which would be produced by the exact ground state solution of the Schrödinger equation. Finding the energy functional minimum therefore guarantees the solution for the exact electron density of the system. The exact form of the energy functional is unknown and remains a current challenge of DFT methods today. The energy functional, in terms of the electron density $n(r)$, can be written as:

$$E(n) = T_e(n) + V_{\text{ext}}(n) + V_H(n) + E_{xc}(n)$$ (2.5)

where $T_e(n)$ is the Kohn-Sham kinetic energy, $V_{\text{ext}}(n)$ is the external potential acting on the interacting system, and $V_H(n)$ is the Hartree Energy. The term $E_{xc}$ is known as the
exchange-correlation functional and includes the effects of exchange and correlation interactions between electrons as well any other effects, such as self-interaction corrections, which are not included in other known terms. Other than for free electron gas systems, the exact form of the exchange-correlation functional is not known. Several approximate forms are used for this term instead, such as the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA). LDA is the most basic approach and uses the local density of the exactly known uniform electron gas, whereas GGA is slightly more sophisticated and incorporates the local gradient of the electron gas, in addition to the local density. There exists numerous variations of these functionals, as well more complex hybrid functionals that incorporate additional terms.

The time-independent Schrödinger equation may be formulated in terms of the electron density using the energy functional described by Equation 2.5:

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(r) + V_H(r) + V_{XC}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r) \tag{2.6}
\]

Impressively, this new formulation of the time-independent Schrödinger equation is a function of only three spatial variables, whereas Equation 2.1 is a function of 3N variables. The exchange-correlation functional is related to the term \( V_{XC}(r) \) by

\[
V_{XC}(r) = \frac{\delta E_{XC}(r)}{\delta n(r)} \tag{2.7}
\]

Iteratively solving for the electron density using the Kohn-Sham equations allows to obtain a self-consistent solution for the ground state energy.

### 2.1.4 Plane-wave periodic systems

Continuous periodic systems, such as solid crystalline structures, can be modelled by periodically repeating an irreducible unit, known as a supercell. For such periodic systems, the solution to Schrödinger’s equation must satisfy Bloch’s theorem. According to Bloch’s theorem, for period systems such as crystalline structures, there exists a basis set of wavefunctions such that the wavefunctions may be written as

\[
\psi_k(r) = \exp(i \mathbf{k} \cdot \mathbf{r}) u_k(r) \tag{2.8}
\]

where \( u_k(r) \) has the same periodicity as the crystal structure. This formulation implies that the Schrödinger equation may solved for each value of \( \mathbf{k} \) independently. The \( k \)-space basis set, also known as reciprocal space, in which the \( \mathbf{k} \) vector exists, naturally lends itself to describing periodic systems compared to using the spatial coordinates that define
Euclidean space. Working with systems in $k$-space may be referred to as plane wave calculations as they exploit the plane-wave basis set ($u_k(r)$ in Equation 2.8 denotes a plane wave function). Many DFT calculations involve integrating functions of $k$ vectors over the primitive cell of the system in $k$-space. The latter is also known as the Brillouin zone, and the selection of $k$ values over which to perform integration in the Brillouin zone is a key parameter that must be specified in all DFT calculations.

The periodicity of the $u_k(r)$ term in Equation 2.8 allows for it be further expanded in terms of a set of plane waves such that

$$u_k(r) = \sum_G c_G \exp(iG \cdot r)$$

(2.9)

where the set of reciprocal-space vectors $G$ is defined so that for any real space lattice vector, $a_i$, $G \cdot a_i = 2\pi m_i$, where $m_i$ is an integer value. Combining this equation with Equation 2.8 gives

$$\psi_k(r) = \sum_G c_{G+k} \exp[i(k + G)r]$$

(2.10)

Although this expression involves a summation over an infinite number of $G$ vector values, the functions in Equation 2.10 can be interpreted as solutions of the Schrödinger equation containing kinetic energy, $E = \frac{\hbar^2}{2m} |k + G|^2$. The infinite sum can therefore be truncated to include only solutions which have kinetic energies below a certain cutoff energy, allowing for the expression to be further reduced to

$$\psi_k(r) = \sum_{|G+k| < G_{cut}} c_{G+k} \exp[i(k + G)r]$$

(2.11)

The cutoff energy $G_{cut}$ determines which solutions are to be considered physically relevant to the problem, and is therefore another crucial parameter that must be carefully selected in all DFT implementations.

### 2.1.5 Pseudopotentials

The contribution of an atom’s core electrons is often insignificant compared to that of the valence electrons. When modelling the physical interactions between atoms, core electrons often require very large energy cutoffs in plane wave calculations due to their small length scale oscillations. To address this inefficiency, the core electrons of atoms in a system can be approximated by pseudopotentials which consists of assigning an effective density to electrons under a certain radial cutoff. This approach simultaneously allows
for the selection of a significantly lower energy cutoff, and for the size of the system to be reduced as only valence electrons are considered. A variety of pseudopotentials are available for DFT implementations, the three most common types being the ultrasoft pseudopotentials (USPP) [30], the projected augmented wave (PAW) [31], and the norm-conserving pseudopotentials.

### 2.2 Nudged Elastic Band Method

Transition state theory tells us that the rate of a chemical reaction is dependent on an activation energy barrier, which may be expressed by the Eyring equation:

$$k = \frac{k_B T}{h} \exp \left( -\frac{\Delta G_a}{RT} \right)$$

(2.12)

where $\Delta G_a$ is Gibbs free energy of activation, $k_B$ is Boltzmann’s constant, $h$ is Planck’s constant, $R$ is the gas constant, and $T$ is the absolute temperature. The Gibbs free energy of activation, $\Delta G_a$, is the energy difference between the energy minimum and the transition state of the reaction (Figure 2.1).

![Figure 2.1: Schematic depicting the free energy curve for the reaction involving the progression of a system from state A to state B along an arbitrarily defined reaction coordinate, with activation energy $\Delta G_a$.](image)

It is therefore of interest to determine the activation barriers of reactions. However, given that DFT follows an energy minimization algorithm, we require other numerical methods to find transition states. The Nudged Elastic Band (NEB) technique is one such method for finding the Minimum Energy Pathway connecting two local minima on a potential energy surface [32]. The activation barriers and transition states associated with the reaction can then be obtained from the minimum energy pathway. The NEB method
works by first linearly interpolating a set of images between the system’s initial and final states, and then minimizing the energy of the interpolated images while subjecting them to a set of force constraints. \[33\] The total energy of the images along the reaction coordinate can be written as:

\[
M(r_1, r_2, ..., r_{N-1}) = \sum_{i=1}^{P-1} E(r_i) + \sum_{i=1}^{P} \frac{K}{2} (r_i - r_{i-1})^2
\]  

(2.13)

where \(E(r_i)\) and \(\frac{K}{2} (r_i - r_{i-1})^2\) are the intrinsic and spring energies, respectively, for the \(i\)th image within the set of images \((r_1, r_2, ..., r_{N-1})\). Minimizing the function \(M(r_1, r_2, ..., r_{N-1})\) pushes the images closer to the minimum free energy pathway. The force minimizing the energy of each image is taken as \(F_i = -\nabla E(r_i)\), where \(E(r_i)\) is obtained from a ground-state DFT calculation. To prevent the images from moving to their minimum energy configurations, as would be the case in a regular DFT calculation, only the force component perpendicular to the direction of the path, \(\hat{\tau}_i\) is applied to minimize the energy of the image:

\[
F_{i}^\perp = F_i - (F_i \cdot \hat{\tau}_i)
\]  

(2.14)

where \(\hat{\tau}_i\) is the direction defined by the line connecting images \(i + 1\) and \(i - 1\) (Figure 2.2). Spring forces are also added to maintain the distance between neighboring images along the path while their energies are minimized. To prevent the images from moving away from the minimum energy pathway, only the component of spring force parallel to the direction of the path is taken:

\[
F_{i,\text{spring}}^\parallel = \left\{ [K(r_{i+1} - r_i) - (r_i - r_{i-1})] \cdot \hat{\tau}_i \right\} \hat{\tau}_i
\]  

(2.15)

where \(K\) is the spring constant. The net force on each image is then computed at each iteration, and the energy and location of each image along the pathway is updated accordingly.

\[
F_{i,\text{update}} = F_{i}^\perp + F_{i,\text{spring}}^\parallel
\]  

(2.16)

The images converge to the minimum energy path once the net force on acting on each image is zero (Figure 2.2).

The addition of the Climbing Image (CI) implementation to the NEB method allows for locating the saddle point along the minimum energy pathway, as there is no guarantee of an image converging to this point in the basic NEB method. \[33\] In the CI-NEB
method, the highest energy image is forced to the location of the saddle point by replacing the spring forces acting on the image with an inverted version of the true force that acts tangent to the path at this point. This results in the image trying to maximize its energy, forcing it towards the maximum point along the minimum energy pathway, while still minimizing its potential energy in the directions perpendicular to the path. [33]

2.3 Ab Initio Molecular Dynamics

While the previously described NEB and CI-NEB methods provide the means to obtain the minimum energy pathway of a reaction, they are still static approaches in which atomic configurations assume their lowest ground state energies. Molecular dynamics (MD) is a technique that allows to simulate the evolution of system’s trajectory while simultaneously accounting for the electronic effects (ie. quantum mechanical effects) as well as ionic effects (ie. the motion of atoms). The MD algorithm involves calculating the potential energy of the system, using this potential to compute the forces acting on each atom, and then advancing the positions of the atoms over some specified time interval using Newton’s equations of motion. The general algorithm for classical MD is illustrated in Figure 2.3.

Temperature can be sampled based on ensemble averages derived from statistical
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Figure 2.3: Basic Molecular Dynamics (MD) algorithm. [34].

thermodynamics. Here we use the canonical ensemble \((N,V,T)\), corresponding to the Helmholtz free energy surface, in which the system temperature is held constant and the system is allowed to exchange energy with its surroundings, as this is a more accurate representation of real world conditions. This was implemented using the Andersen thermostat [35] which assigns velocities to particles based on the Maxwell-Boltzmann distribution for a given temperature.

While classical MD considers atoms as individual hard spheres, ab initio molecular dynamics (AIMD) also considers the quantum mechanical effects of electrons and uses DFT methods to obtain the potential energy and the forces that act on the system at each time step. In the present investigation, we used Born-Oppenheimer molecular dynamics (BOMD), which assumes the electrons and the nuclei to be fully decoupled from each other. A self-consistent electronic ground state DFT calculation is conducted to obtain the potential energy of the system as a function of spatial electron density, and the forces acting on nuclei are then obtained by the Hellmann-Feynmann theorem:

\[
\vec{F}_i = -\frac{dE}{d\vec{R}_i} = -\frac{d}{d\vec{R}_i} \langle \Psi \left| \hat{H} \right| \Psi \rangle = \langle \Psi \left| -\frac{d\hat{H}}{d\vec{R}_i} \right| \Psi \rangle = \langle \Psi \left| -\frac{d\hat{V}}{d\vec{R}_i} \right| \Psi \rangle = (2.17)
\]

These resulting forces are then used to solve the equations of motion of the nuclei, allowing them to be treated similarly to classical particles. Separating the electronic from the nuclear contributions ensure that the evolution of the system follows the Born-Oppenheimer energy surface.
Finally, there exists a variety of numerical schemes used for integrating the equations of motion in order to compute the particle trajectories. The velocity verlet scheme [36], which involves performing numerical integrations such that the positions and velocities are obtained at the same time value, was implemented in the present work.

### 2.3.1 Metadynamics

In order to maintain numerical accuracy in AIMD calculations, simulations must assume very small time steps on the order of 1-2 fs. Given that chemical reaction typically occur on the order of nanoseconds or microseconds, huge computational times and resources are required to fully capture a reaction using AIMD. Other schemes are therefore required to simulate the evolution of a system in a feasible amount of time. Here we used metadynamics (MetaD), a relatively new computational approach that has proven to be a useful tool to overcome the sampling limitations of molecular dynamics of complex molecular processes [37, 38, 39, 40]. In this method, a history-dependent potential is added intermittently throughout the simulation to encourage efficient exploration of the corresponding free energy surface. The latter is defined over a set of collective variables (CVs), which are functions of spatial coordinates carefully selected to provide a complete description of the slow degrees of freedom of the system. The collective variables corresponds to \( S(R), \) which is a set of \( d \) functions of coordinates \( R(\mathbf{r}(t)) \) of the system:

\[
S(R) = \{S_1(R), S_2(R), \ldots, S_d(R)\} \tag{2.18}
\]

The history-dependent bias potentials takes the form of Gaussian functions that are added to the Hamiltonian of the system. At time \( t \), the external potential \( V_G \) is defined as:

\[
V_G(S, t) = W \sum_{t' = \tau_G, 2\tau_G, \ldots \text{ for } t < t'} e^{-\frac{(S(t) - S(t'))^2}{2\delta S^2}} \tag{2.19}
\]

where \( \tau_G \) is the frequency of Gaussian deposition, \( W \) is the Gaussian height, and \( \delta S \) is the Gaussian width. The addition of bias potentials throughout the simulation allows the system to escape beyond high energy barriers, and the free energy surface can thus be reconstructed from the their sum (Figure 2.4). The free energy \( F(S) \) can be represented as a function of the CVs by the following relationship:

\[
F(S) = -k_B T \ln \left( \int dR e^{-\frac{\mathcal{V}(S)}{k_B T}} \delta(S - S(R)) \right) \tag{2.20}
\]
where $k_B$ is the Boltzmann constant, and $T$ is the temperature of the system. In the long time limit ($t \to \infty$), the free energy surface becomes:

$$\lim_{t \to \infty} V_G(S, t) \sim -F(T)$$  \hspace{1cm} (2.21) $$

Figure 2.4: The metadynamics (MetaD) approach: the addition of bias potentials allows the system to escape beyond high energy barriers.

In this work, we employ well-tempered MetaD, which includes an additional tuning parameter to represent the effective sampling temperature of the CV space. [41] In this method, the added Gaussian potentials are rescaled at each step to allow for the net bias to converge more smoothly, and in doing so prevents the simulation from overfilling the free energy surface. In well-tempered MetaD, the bias potentials take the form:

$$V_{G,WT}(S, t) = k_B \Delta T \ln \left[ 1 + \frac{\omega N(S, t)}{k_B \Delta T} \right]$$ \hspace{1cm} (2.22) $$

where $N(S, t) = \int_0^t \delta_{S, S(t')} dt'$ is the histogram of the set of CVs $S$, $\Delta T$ is an added tuning parameter, and $\omega$ is an energy rate. The well-tempered MetaD algorithm is implemented by rescaling the Gaussian height $W$ according to the previously deposited bias potentials:

$$W = \omega \tau_G e^{-\frac{V_G(S, t)}{k_B \Delta T}}$$ \hspace{1cm} (2.23) $$

In the long-time limit ($t \to \infty$), the bias potential converges to

$$V_{G,WT}(S, t \to \infty) = -\frac{T + \Delta T}{\Delta T} F(S) + C$$ \hspace{1cm} (2.24) $$
where $C$ is an nonphysical constant. [40] Introducing the tuning parameter $\Delta T$ limits the exploration of the free energy surface to physically interesting regions on the order of $T + \Delta T$, avoids the risk of overfilling the free energy surface, and guarantees convergence in the long time limit, making well-tempered MetaD a more effective method, operating between the limiting cases of standard MetaD and nonbiased sampling. [41]

2.4 Bader Charge Analysis

NEB and AIMD are both DFT-based approaches that serve to identify the minimum energy pathway of a reaction. While both provide insight into the energy of a system configuration along the reaction pathway, they do not directly describe the charge transfer between atoms. However, DFT calculations still produce the approximate electronic charge distribution throughout a system, from which an estimation of the ionic charges present on atoms and molecules can be extracted. Bader Charge Analysis is a post-processing method to DFT calculations that assigns charge to individual atoms by partitioning the charge density into volumes based on the distribution of charge density. Each volume contains a single local maximum of electron density, and the borders defining adjacent volumes are defined by the zero flux surface of the electron density gradients, $\Delta \rho(\mathbf{r}) \cdot \hat{n} = 0$, where $\rho(\mathbf{r})$ is the electron density and $\hat{n}$ is the unit vector perpendicular to the surface separating each volume (Figure 3.1). For numerical calculations, the charge density is defined in a discretized space, rendering the identification of the zero flux surface difficult. Many algorithms have been developed to efficiently and accurately integrate the electronic density within each atomic volume; however, each method is limited by convergence problems and computational effort requirements. Here we use a Bader analysis program that is based on an algorithm that employs steepest ascent path along the charge density gradient to decouple the electronic contributions of atoms. [42, 43]
Figure 2.5: Bader model for assigning charge to individual atoms. [44, 42, 43]
Chapter 3

Finite Temperature Study on CO$_2$ Reduction over In$_2$O$_3$–$x$(OH)$_y$

3.1 Introduction

In light of climate change and growing global energy demands, the conversion of greenhouse gas CO$_2$ into carbon-based fuels and chemical feedstocks may be the key to building a carbon neutral sustainable economy. [45, 46] The production of fuels, such as CH$_4$ and CH$_3$OH, requires splitting of gaseous CO$_2$, which has led to a widespread investigation by the scientific community to find a cheap and abundant catalyst material capable of efficient C-O bond cleavage. [47, 48] The concept of Frustrated Lewis Pairs (FLPs), in which a sterically hindered Lewis acid-base pair forms a reactive site conducive to the activation of small molecules, offers an effective solution for CO$_2$ activation. [49, 50] Unlike classical Lewis acids and bases that react to form Lewis adducts, the electronically unquenched nature of FLPs accords them a chemistry typically characteristic of transition metals, enabling them to heterolytically split H$_2$ and subsequently react with a variety of species, such as alkenes, aldehydes, and even carbon dioxide. [51, 52] To date, FLP complexes have been demonstrated to reversibly bind CO$_2$ [53, 54], as well as to stoichiometrically reduce CO$_2$ to CH$_3$OH [55, 56, 57, 58], CH$_4$ [59] and CO [60]. Their unique reactivity continues to find applications in new areas, such as transition metal chemistry, bioinorganic chemistry, and materials science. [49, 52] While the notion of FLPs has remained synomymic to molecular FLPs, the existence of FLP sites on the surface of nanocry stalline hydroxylated indium oxide (In$_2$O$_3$–$x$(OH)$_y$) catalyst surface has recently been brought to light. [10, 14, 13] Indium sesquioxide (In$_2$O$_3$) is renowned for its electronic, optical, and surface properties [61, 62]; however, the introduction of
oxygen vacancies and surface hydroxides has been shown to create a promising catalyst capable of converting CO$_2$ to CO via the Reverse Water Gas Shift (RWGS) reaction, CO$_2$ + H$_2$ $\rightarrow$ CO + H$_2$O, at a rate of 150 $\mu$mol g$^{-1}$ hour$^{-1}$. [14] In the RWGS reaction, the surface FLP heterolytically splits gaseous H$_2$ and the resulting proton and hydride moieties are bound to a surface hydroxide group and an indium atom, creating a site suitable for CO$_2$ capture and reduction. In this process CO$_2$ is converted CO and H$_2$O, which desorb to leave behind surface FLP sites accessible for further reactions (Figure 3.1).

Figure 3.1: Overall mechanism for the RWGS reaction on In$_2$O$_{3-x}$(OH)$_y$, as derived from ground state DFT calculations. [14]

The rate of conversion of CO$_2$ to CO has been found to be four times greater under visible light conditions and theoretical studies of ground and excited states have confirmed surface FLP chemistry to be key in driving both the thermochemical and photochemical reactions. [14, 13] In visible light, catalytic activity has been reported to increase from 15.4 $\mu$mol g$^{-1}$ hour$^{-1}$ at 150 °C to 153 $\mu$mol g$^{-1}$ hour$^{-1}$ at 180 °C, beyond which point the catalyst is reportedly no longer stable due to sintering of the nanoparticles. In dark conditions, practicable CO production is achieved at 165 °C and increases to 35.7 $\mu$mol g$^{-1}$ hour$^{-1}$ at 180 °C (Figure 3.2). [14]

While a multistep mechanism for the RWGS reaction based on ground state density functional theory has been proposed, it does not capture changes in reaction paths that may proceed at finite temperature and the corresponding influences on energy barriers
Figure 3.2: (A) Temperature dependence of CO production for In$_2$O$_{3-x}$ (OH)$_y$ nanoparticle catalysts under flowing H$_2$ and CO$_2$. (B) Pseudo-Arrhenius plots drawn from temperature dependent measurements. [14]
owing to entropic effects. In this study we use well-tempered metadynamics-biased ab initio molecular dynamics to explore the free energy Surface of surface FLP induced $H_2$ splitting, $CO_2$ reduction, and $H_2O$ desorption over $In_{2}O_{3-x}(OH)_y$ with the objective of identifying the minimum free energy pathways, the corresponding activation energies, and the rate limiting step of the reaction at finite temperatures. In addition, we provide grounds for the enhanced activity of the thermochemical RWGS reaction observed experimentally at higher temperature, derived from the thermal effects on surface FLP chemistry.

### 3.2 Literature Review

FLPs have proven to be molecular complexes capable of overcoming the large kinetic barrier required for the dissociation of the C-O bond on the $CO_2$ molecule. In [57], the $R_3P/AIX_3$ (where $X=I, Br, Cl$) was found to react, via both experimental and computational methods, with $CO_2$ to form $R_3PC(OAIX_3)$, and further reaction with $CO_2$ produced CO. It is suggested that effective catalytic reduction of $CO_2$ will require a less oxophilic Lewis acid on the FLP site.

In [55], both computational and experimental investigations revealed that $CO_2$ may be reduced to methanol via a mechanism that also employs FLPs. In contrast to the results in [57], the FLP site was found to be involved in every step of the mechanism, and the oxophilic nature of the Lewis acid was not reported to influence the rate of reaction. The present study involves probing the reduction of $CO_2$ to CO via FLP sites on the surface of hydroxylated indium oxide, and the results to date show that clogging of $H_2O$ molecules on the catalyst surface impedes subsequent reactions, thus diminishing the rate of reaction over time. [57] suggests that the oxyphilicity of the surface may therefore be an important factor.

AIMD has been demonstrated to be a useful technique to explore catalytic reaction pathways. [63] investigated the electrochemical reduction of $CO_2$ to CO via a cobalt porphyrrun catalyst in aqueous media. They employed AIMD, in conjunction with umbrella sampling, to study the deprotonation of $CoPCOOH$ and the C-OH bond activation of $CoPCOOH$. Both steps were found to possess low activation barriers and are energetically favourable, an indication that the rate limiting step lies in the transfer of an electron from the electrode to the catalyst. [38] used metadynamics-biased AIMD simulations to investigate the hydrogenation of $CO_2$ via a ruthenium dihydride catalyst. The insertion of $H_2$ following the $CO_2$ was found to be the rate-limiting step, regardless of whether the catalyst takes a cis or trans isomerization. Based on the computed transitions states
and their corresponding electronic structures, it was revealed that catalytic activity is determined primarily by the electronic structure of the intermediate complex, rather than by steric hindrance.

While the papers explore different catalytic reactions, both demonstrate how AIMD calculations can be used to understand the interaction of CO$_2$ with a catalyst complex. [63] investigated the electrochemical reduction of CO$_2$; in the process, the experiments identified the intermediate complexes, which may extend to the thermal reduction of CO$_2$, the focus of the present MetaD-biased AIMD study. In [38], it was shown that MetaD-biased AIMD can be used to explore the free energy surface of a reaction. This technique is also recommended by [63] as the computational tool of choice for further CO$_2$ reduction studies.

### 3.3 Computational Details

#### 3.3.1 Methods

In order to investigate the reaction mechanism at finite temperature, we performed ab initio molecular dynamics (AIMD) on the Born Oppenheimer surface. Throughout the study, AIMD simulations were performed with the Quantum Espresso software package [64] using the DFT plane-wave basis set approach. All calculations were spin-polarized and implemented using the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional [65], together with the Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) ultrasoft pseudopotentials [30]. Kinetic energy cutoffs were 50 Ry and 400 Ry for the wavefunctions and charge density, respectively; and the criterion for self-consistent field convergence was set to $1 \times 10^{-6}$ Ry. Brillouin zone integrations were performed over the gamma point due to the large size of the supercell. After converging the complete structure at ground state configuration initially, the bottom two layers were frozen in all AIMD calculations, while the top two layers and adsorbants were allowed to relax. Relaxation was performed using the conjugate gradient minimization algorithm until the magnitude of the residual Hellman-Feynman force on each atom was less than $1 \times 10^{-3}$ Ry/Bohr. The Anderson thermostat was used to maintain temperature in all simulations. Each reaction step was investigated at 20 $^\circ$C, in order to gain insight into its room temperature feasibility, and at 180 $^\circ$C, which has been reported to be the temperature yielding highest activity. [14] Moreover, changes to the minimum reaction energy pathway, and their concomitant effects on transition state structures, that result from increased thermal energy were captured by performing the simulations at different temperatures. A
time step of 2.0 fs was taken for all AIMD simulations. This value was determined by performing multiple test simulations as large enough to minimize computational cost of sampling the free energy surfaces, yet sufficiently small to guarantee the accuracy of the Verlet algorithm. Well-tempered MetaD-biased simulations were carried out using the PLUMED plug-in. Bader charge analysis was used to obtain an approximation of the relative charges associated with individual atoms. [42, 43]

3.3.2 Model

DFT calculations were performed on the (111) surface of In$_2$O$_{3-x}$(OH)$_y$; the surface was selected based on previously obtained TEM images of nanocrystalline In$_2$O$_{3-x}$(OH)$_y$ samples, as well as theoretical studies revealing (111) to be the thermodynamically favored surface of In$_2$O$_3$. [14, 66] A 161-atom four layer slab with a 20 Å vacuum was used to model the surface, as shown in Figure 3.3.

![Figure 3.3: Side view of the In$_2$O$_{3-x}$(OH)$_y$ supercell. The light blue atoms denote indium, the red atoms denote oxygen, and the dark blue, hydrogen.](image)

3.4 Results and Discussion

The RWGS reaction mechanism over In$_2$O$_{3-x}$(OH)$_y$ has previously been identified to occur via two steps: H$_2$ is first dissociately adsorbed by the surface FLP site, and CO$_2$ is
Chapter 3. Finite Temperature Study on CO$_2$ Reduction over In$_2$O$_{3-x}$(OH)$_y$

subsequently adsorbed and dissociated. In order to capture the details of each reaction step, separate metadynamics-biased simulations were performed for H$_2$ splitting and CO$_2$ reduction.

3.4.1 Hydrogen Dissociation via Surface FLP

The dissociation of H$_2$ over the catalyst surface at 20 °C and 180 °C was investigated using well-tempered MetaD-biased AIMD. Several test runs were first performed to optimize the various simulation parameters, i.e. the number and type of collective variables, the molecular dynamics time-step, as well as the height and width of the Gaussian bias potentials. Two collective variables, CV1 and CV2, were selected to ensure a complete and relevant representation of the free energy surface. CV1 is defined as the distance from the Lewis acid acting In (labeled In28) on the surface to the nearest H (labeled H1) on the adsorbant hydrogen molecule, while CV2 corresponds to the distance from O on the surface hydroxyl group (labeled O1) to the other H (labeled H2) on the adsorbant hydrogen molecule, as shown in Figure 3.4. No constraints were placed on the system in the first simulation, and bias potentials 0.1 eV in height were applied intermittently over the course of 42 fs. Based on the area of the free energy surface explored in the first simulation, three constraints were introduced to ensure exploration of the region relevant to the reaction: an upper wall limiting the distance from O1 to H2 to a maximum of 2 Å, a lower wall limiting the distance from H2 to In28 to a minimum of 1.8 Å, and another lower wall limiting the distance from H1 to H2 to a minimum of 0.74 Å. Gaussian bias potentials of height 0.05 eV were deposited over the course of 32 fs for the latter, at which point dissociation was visibly achieved. The free energy surface was generated by two separate simulations, both employing a tuning parameter of 7000, a bias factor of 6, Gaussian widths of 0.1, and bias potentials placed every 30 iterations.

The free energy surface (Figure 3.5, top) corresponding to 20 °C shows the dissociative adsorption of hydrogen to have an energetic barrier of 0.36 eV and a Gibbs free energy of reaction of 0.16 eV. This matches with previously reported results that were derived from ground state DFT reaction path finding methods that showed the dissociative adsorption of H$_2$ on In$_2$O$_{3-x}$(OH)$_y$ to be endothermic. In this mechanism, the hydrogen molecule approaches the surface FLP site until it becomes sufficiently polarized and dissociates, at which point the hydrogen moieties become bound to oxygen on a surface hydroxyl group and to a neighboring surface indium atom, as shown in Figure 3.6. The hydrogen molecule floating over the catalyst surface has an initial bond length of 0.78 Å (Figure 3.6), and becomes stretched to 1.01 Å at the transition state (Figure 3.5), at which point
Figure 3.4: CVs used to define the free energy surface; CV1 is defined as the distance from the Lewis acid acting In (In28) to the nearest H (H1) on the adsorbate hydrogen molecule, while CV2 corresponds to the distance from O on the surface hydroxyl group (O1) to the other H (H2).
Figure 3.5: Free energy surfaces generated from MetaD-biased AIMD simulations for H₂ dissociation at 20 °C (top) and 180 °C (bottom). Points A and B denote locations of energy minima, and triangles TS denote locations of transition states.
it dissociates into two H atoms, which subsequently get attached to the OH group and the neighboring In sites, respectively, as shown in Figure 3.6. In agreement with previously reported ground state DFT results, Bader charge analysis, which is further discussed below, revealed the dissociation of H₂ to be heterolytic in nature.

Figure 3.6: Atomic configurations corresponding to states A, TS, and C (Figure 3.5, top) for the dissociation of H₂ at 20 °C. Frame A corresponds to the reactant state, frame TS to the transition state, and frame C to the dissociated product state. Light blue denotes In, red denotes O, and dark blue denotes H.

Figure 3.7: Atomic configurations corresponding to states A, TS1, B, TS2, and C (Figure 3.5, bottom) for the dissociation of H₂ at 180 °C. Frame A corresponds to the reactant state, frame B to the intermediate state, and frame C to the dissociated product state. Light blue denotes In, red denotes O, and dark blue denotes H.

At a higher temperature of 180 °C, the dissociation of H₂ molecule was found to proceed in two sub-steps, as shown in Figure 3.7. The H₂ adsorbate first approaches the surface and interacts with the Lewis-acting surface In atom to form transition state (TS1) in which the H₂ bond is stretched to 0.86 Å (TS1 in Figure 3.7). The distance from H₂ to the surface In is subsequently reduced (1.84 Å), while the distance to the surface hydroxyl group is further diminished (1.64 Å), forming a stable intermediate that was not observed at 20 °C (B in Figure 3.7). An explanation for the presence of an intermediate state at 180 °C is offered below. From intermediate state B, the reaction proceeds over a second transition state (TS2 in Figure 3.7), similarly to the mechanism at 20 °C. The hydrogen
molecule subsequently dissociates, and the resulting fragments are bound to the surface Lewis acid and Lewis base sites, identical to the room-temperature mechanism, reported before [14]. The free energy surface (Figure 3.5, bottom) shows that these sub-steps have energy barriers of 0.11 eV and 0.20 eV, respectively. The Gibbs free energy of reaction is net reaction is 0.13 eV, suggesting that the reaction proceed more favourably at 180 °C, which agrees with previously reported experimentally-derived temperature-dependent rate measurements. [14]

![Figure 3.8: Frustrated Lewis pair site on the surface of In$_2$O$_{3-x}$(OH)$_y$.](image)

According to transition state theory, the increased likelihood of the adsorbant colliding with the surface due to temperature is not expected to influence the topology of the free energy surface. Indeed, the appearance of an intermediate reaction step reveals a difference in the nature of the interaction between the adsorbant hydrogen molecule and the surface FLP site at higher temperature. To understand this further, two unbiased AIMD simulations were performed, one at 20 °C and the other at 180 °C, over 584 ps to compare the evolution of FLP structure. The distance from the Lewis base acting O on the hydroxyl group to the Lewis acting indium atom 3.8 was tracked over the course of the simulations to obtain a time-average FLP bond length. As expected by Boltzmann statistics, the fluctuations in FLP bond length were slightly greater in the higher temperature simulation (0.04 Å at 20 °C, compared to 0.05 Å at 180 °C); however, the time-average FLP bond length was also found to increase, from 3.35 Å at 20 °C to
3.39 Å at 180 °C, indicating a thermally-induced change to the lattice structure. The alteration to the free energy surface for the dissociation of H₂ at 180 °C can likely be attributed to the enhanced separation of the surface FLP resulting at this temperature. To confirm this, the FLP bond distance was measured to be 3.28 Å at the intermediate state that appears at 180 °C (state B, Figure 3.7), whereas the structure corresponding to the equivalent set of CVs at 20 °C has a FLP bond distance of 3.25 Å. While this difference in bond length might appear minute, it is, to the best of our knowledge, the largest observable difference between equivalent regions of the free energy space at 20 °C and 180 °C, and may therefore be the key to creating the conditions for intermediate state that appears at 180 °C (B in Figure 3.7). At both temperatures, the region of the free energy surface relevant to the dissociation of H₂ was observed to be dependent on CV2 (i.e. the distance from the O on the surface -OH group to nearest H on H₂) and independent of CV1 (i.e. the distance from the surface In to the nearest H on H₂). The terminally-bonded nature of surface hydroxyl group enables it with greater rotational degrees of freedom as compared to the highly coordinated Lewis acid acting In that is embedded in the top layer of the lattice structure. The movement of surface hydroxyl group is therefore more likely to drive the increase in separation between the FLP that results at higher temperature, compared to the surface In site. This view offers an explanation for the distance between the hydrogen molecule to the surface hydroxyl group (CV2) being the reaction-driving variable.

Bader Charge Analysis

Table 3.1: Bader charge analysis performed comparing the charge associated with the adsorbate hydrogen molecule (H1,H2) and the Lewis acid (In) and Lewis base (O) sites on the surface, immediately before and after H₂ dissociation at 20°C and 180°C.

<table>
<thead>
<tr>
<th></th>
<th>In₂O₃₋ₓ(OH)ᵧ and H₂ before splitting</th>
<th>In₂O₃₋ₓ(OH)ᵧ after H₂ splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20°C</td>
<td>180°C</td>
</tr>
<tr>
<td>H1</td>
<td>-0.24</td>
<td>-0.22</td>
</tr>
<tr>
<td>H2</td>
<td>0.25</td>
<td>0.21</td>
</tr>
<tr>
<td>In28</td>
<td>1.70</td>
<td>1.69</td>
</tr>
<tr>
<td>O1</td>
<td>-1.24</td>
<td>-1.68</td>
</tr>
</tbody>
</table>

Bader charge analysis conducted immediately prior to hydrogen dissociation reveals that the Lewis acidic In and Lewis basic O of the OH sites at the surface possess charges of +1.70e and -1.24e at 20 °C and +1.69e and -1.68e at 180 °C (Table 3.1). The frustrated charges of the surface FLP pair generate an electric field that polarizes the H molecule...
as it approaches the surface. The nearby H being more positively charged that the Lewis acid acting In accepts the excess charge from the latter and thus attains a negative charge of -0.36e and -0.37e at 20 °C and 180 °C, respectively. The other H, being closer to the Lewis base acting O on the surface -OH group is more negatively charged and donates its charge to obtain a charge of +0.78e and +0.64e at 20 °C and 180 °C, respectively. These results confirm the heterolytic nature of H₂ splitting and match those previously reported [14] for the ground state mechanism. The charge present on the Lewis acid acting In remains very consistent with temperature. While the O on the Lewis base acting hydroxide appears more negatively charged (-1.68e) at 180 °C, the net charge of the hydroxyl group (ie. the combined charge of O and H on OH) does not change with temperature (-0.64e and 0.69e at 20 °C and 180 °C, respectively).

Given the previously discussed observation of the average FLP bond distance being greater at 180 °C, further analysis was conducted to investigate a potential correlation between FLP bond distance (Figure 3.8) and the charges present on the Lewis acid and Lewis base sites. Bader Analysis was conducted to obtain the charges on the Lewis acid-acting In and the Lewis-base acting O on OH for FLP bond distances ranging from 3.32 Å to 3.40 Å. The net charge of OH was considered as the Lewis base charge, as the analysis cannot reliably distinguish the charge associated to O from that associated to the H on the surface hydroxyl group. Table 3.2 shows that the charge associated to the FLP sites remains consistent with FLP bond distance. The slightly increased degree of polarization present measured at 3.40 Å is likely negligible. Despite no apparent relation between the distribution of charges on the FLP sites for different separation lengths, larger FLP bond lengths may still be advantageous for activating H₂ as more interaction space in between the Lewis acid and base becomes available.

Table 3.2: Charges computed on the Lewis acid and Lewis base sites with varying FLP bond distance.

<table>
<thead>
<tr>
<th>FLP Distance (Å)</th>
<th>In</th>
<th>OH</th>
<th>Charge Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.32</td>
<td>1.54</td>
<td>-0.68</td>
<td>2.21</td>
</tr>
<tr>
<td>3.34</td>
<td>1.54</td>
<td>-0.68</td>
<td>2.22</td>
</tr>
<tr>
<td>3.35</td>
<td>1.54</td>
<td>-0.68</td>
<td>2.21</td>
</tr>
<tr>
<td>3.38</td>
<td>1.54</td>
<td>-0.68</td>
<td>2.22</td>
</tr>
<tr>
<td>3.40</td>
<td>1.57</td>
<td>-0.67</td>
<td>2.24</td>
</tr>
</tbody>
</table>

### 3.4.2 CO₂ Adsorption and Dissociation

The subsequent step in the RWGS catalytic reaction proposed by Ghuman et al. [?] is the capture and reduction of CO₂ at the In₂O₃₋ₓ(OH)ₙ surface. This reaction was
also investigated at 20 °C and 180 °C using well-tempered MetaD-biased AIMD. Test simulations were first performed to optimize the various simulation parameters, as the dissociation of H₂. The two CVs that capture the energetics of this reaction are shown in Figure 5: CV1 corresponds to the angle formed by the CO₂ molecule (specifically, the angle formed by O1, C1, and O2 as shown in Figure ??), while CV2 is the distance from C1 to a point the midpoint between two neighboring surface indium atoms (labeled In28 and In60). A series of simulation were performed to capture the free energy surface of the adsorption and reduction of CO₂. Similar as for H₂ dissociation, simulations were first performed with the purpose of roughly exploring the free energy surface, followed by others to achieve finer treatment of the region of interest. In the first simulation, bias potentials of height 0.3 eV were deposited with the distances from O2 to H1 constrained to a maximum of 1.2 Å. In the second, bias potentials of height 0.1 eV were deposited with an additional constraint forcing the distance from O2 to the surface to a maximum of 3.2 Å. In the third and fourth simulations, Gaussian bias potentials of height 0.1 eV were also deposited; however, the constraint on the distance from O2 to the surface was decreased to 2.8 Å. A final run was performed with no constraints placed on the system using 0.1 eV bias potentials. The combination of the various simulations modeled the reaction over a total of 148 fs at 20 °C, and 178 fs at 180 °C. Bias potentials were placed every 30 iterations for all runs. Gaussian widths of 0.1, a bias factor of 6.0, and a tuning parameter of 10,000 were employed for all simulations. The free energy surfaces generated (Figure 3.10) reveal no significant change in the reaction mechanism between 20 °C and 180 °C, other than minor differences in the energetic barrier heights. At both 20 °C and 180 °C, the entire reaction is achieved in three steps that correspond to CO₂ adsorption, deformation, and ultimate dissociation, with transition states indicated by TS1, TS2, and TS3 in Figure 3.10. Under both temperature conditions, the linear CO₂ adsorbate molecule approaches the surface and inserts into the In-H bond, which was produced by the previous dissociative adsorption of hydrogen. It is interesting to note that, by this description, the reaction follows an Eley-Rideal mechanism, as the adsorbate-surface interactions are required to proceed in sequence.

The excess electrons on the hydride interact with the nucleophilic O on CO₂, causing the C-O bond to lengthen from 1.20 Å(state A, Figure 3.11), to 1.26 Å(state B, Figure 3.11), and finally to 1.46 Å(state C, Figure 3.11). The destabilization of CO₂ is further characterized by the bending of the O-C-O bond, from 176°(state A, Figure 3.11) to 151°(state B, Figure 3.11), and finally to 112°(state C, Figure 3.11), at which point the molecule splits to produce H₂O and CO. These findings are consistent with the ground state DFT results reported by Ghuman et al. [14] that showed the initially linear CO₂
The bond angle to become 125.2° and the C-O bond to lengthen to 1.29 Å.

The topology of free energy surface at 180 °C shows a slightly widened reaction pathway compared to that at 20 °C (Figure 3.10), displaying the expected increase in thermal vibrations, as $k_B T$ is equal to 0.025 eV at 20 °C and 0.039 eV at 180 °C. The energy barrier to transition from state A to state B (Figure 3.11) is higher at 20 °C (0.32 eV) compared to 180 °C (0.19 eV), which can be attributed to a higher likelihood of the adsorbate successfully colliding with the surface at higher temperature. The subsequent energy barriers, corresponding to TS2 and TS3 (Figure 3.10), do not differ sufficiently between 20 °C and 180 °C to observe a significant thermal effect, as the resolution of the free energy surfaces is limited by the height of the deposited Gaussian potentials. The energy barrier associated to the adsorption of CO$_2$ and its initial interaction with surface hydride is therefore found to be reduced at higher temperature, while the later barriers associated to the bending and splitting of the CO$_2$ molecule remain mostly unchanged, suggesting that thermal effects may be relevant only when adsorptive mechanisms are involved. In agreement with previously reported results [14], CO$_2$ adsorption and dissociation is found to be the rate-limiting step of the reaction, with net energetic barriers of 0.93 eV and 0.63 eV at 20 °C and 180 °C, respectively. The Gibbs free energy of the net reaction is remarkably reduced from 0.41 eV at 20 °C, to 0.10 eV at 180 °C, which matches previously reported experimental results showing the reaction to proceed more
Figure 3.10: Free energy surfaces generated using MetaD-biased AIMD simulations for the adsorption and reduction of CO$_2$ over In$_2$O$_{3-x}$(OH)$_y$ at 20 °C (top) and 180 °C (bottom); points A, B, C, and D denote locations of energy minima, and triangles TS1, TS2, and TS3 denote locations of the transition states.
Figure 3.11: Atomic configurations corresponding to states A, B, C, and D (Figure 3.10) for the adsorption and reduction of CO$_2$ at 20 °C and 180 °C. Light blue denotes In, red denotes O, and dark blue denotes H.
readily at higher temperatures. [14]

3.4.3 Dissociative adsorption of H$_2$O

The desorption of H$_2$O is critical to guarantee sustained catalytic activity; water molecules bound to the surface, following CO$_2$ dissociation, will otherwise block catalytic sites and prevent subsequent reactions from taking place. Ghuman et al. report reduced CO production when H$_2$O was introduced into the reactor, under both batch and flow conditions, suggesting that product H$_2$O acts as a reaction inhibitor. [14] The interaction of H$_2$O with the In$_3$O$_{3-x}$(OH)$_y$ surface at both 20 °C and 180 °C was investigated using well-tempered MetaD-biased AIMD. Test runs were first performed to optimize the various aforementioned simulation parameters, and two CVs over which to define the free energy surface were selected (Figure 3.12): CV1 is defined as the distance from In60 on the surface to O2, while CV2 is the distance from In28 to O1. Four simulations were performed to capture the diffusive behavior of H$_2$O at the surface. In the first simulation, Gaussian bias potentials of height 0.3 eV were deposited, with no force constraints applied to the system. In the second, forces limiting the distance from O1 to In28 to 2.08 Å, and the distance from O1 to H2 to 1.22 Å, were introduced. In the third and fourth simulations, the height of the Gaussian potentials was reduced to 0.1 eV, and the constraint on the distance between O1 and H2 was increased to 2.75 Å. The combination of the simulations modeled the reaction over the course of 242 fs at 20 °C, and 259 fs at 180 °C. Gaussian bias potentials of width 0.1 were deposited every 30 iterations and a bias factor of 6 and a tuning parameter of 10,000 were applied in all simulations.

The reconstructed one dimensional free energy surfaces are shown in Figure 3.13. The minimum reaction pathway traced from state A to B via TS corresponds to the transfer of H (on In-bound H$_2$O) to the neighboring surface hydroxyl group, effectively switching the positions of the surface bound H$_2$O and OH groups by a proton-hopping process. The energy barriers corresponding to this step are found to be 0.68 eV at 20 °C and 0.52 eV at 180 °C, revealing the dissociative adsorption to be more favorable than direct desorption of H$_2$O from the surface. Such a result is consistent with previous first-principles studies that showed the dissociative chemisorption of H$_2$O to be favorable on the In$_2$O$_3$ surface. [67] From energy minimum A, energy barriers of at least 1.1 eV and 0.98 eV at 20 °C and 180 °C, respectively must be overcome for desorption of H$_2$O to be achieved. Given these barriers are greater than those the limiting the RWGS reaction, even when temperature conditions considered, the blocking of catalytic sites by product H$_2$O is the likely mechanism preventing sustained catalytic activity over time.
Figure 3.12: CVs used to define the free energy surface; CV1 is defined as the distance from In60 on the surface to O2, while CV2 is the distance from In28 to O1.

For practical purposes, this issue can be circumvented by careful design of a flow reactor in which the product water molecules are removed from the active catalyst surface.

3.4.4 Summary of Reaction Energetics

We performed well-tempered Metad-biased AIMD simulations to investigate the mechanism for the RGWS reaction over the In$_2$O$_{3-x}$(OH)$_y$ surface at temperatures of 20 °C and 180 °C. Free energy surfaces mapping the reaction pathways, transitions states, and locations of energy minima were generated to obtain the energetics for the activation of hydrogen and the capture and reduction of carbon dioxide. The energy barrier associated to the activation of gaseous hydrogen over the surface FLP site was found to be reduced by 0.15 eV at 180 °C (blue line in Figure 3.14), which is substantially lower than at the ground state (pink line in Figure 3.14) reported before.

3.4.5 Bi-Doping

An additional MetaD-biased AIMD simulation was performed to investigate any changes to the H$_2$ dissociation reaction mechanism that may ensue from doping In$_2$O$_{3-x}$(OH)$_y$ with Bi. The simulation was performed at 180 °, with CVs and all other parameters identical to the simulation carried out for H$_2$ on the original In$_2$O$_{3-x}$(OH)$_y$ surface. Bi-
Figure 3.13: Free energy surfaces generated from MetaD-biased AIMD simulations for H₂O adsorption on the surface of In₂O₃₋ₓ(OH)ₙ at 20 °C (top) and 180 °C (bottom). Points A and B indicate locations of energy minima, and triangles TS indicate the locations of a transition state.
Figure 3.14: Summary of energetic barriers for the RWGS shift reaction over In$_2$O$_{3-x}$(OH)$_y$ at 20 °C (pink line) and 180 °C (blue line). The atomic configurations corresponding the each reaction step are shown, with red denoting O, dark blue denoting H, light blue denoting In, and green denoting C.

Figure 3.15: Snapshot of the Bi-doped In$_2$O$_{3-x}$(OH)$_y$ surface prior to H$_2$ dissociation. The purple atom denotes In, the red atoms denote O, and the dark blue atoms denote H.
doping may reduce the propensity of the surface to attract product H\textsubscript{2}O and may could potentially enhance surface reactivity. In this simulation Bi-doping was modelled by replacing the Lewis acid-acting In with Bi (Figure 3.15); however, further studies will be required to test the effect of different surface sites. The Free Energy surface for H\textsubscript{2} dissociation over the Bi-doped FLP site (Figure 3.16) shows the activation barrier to be reduced to three smaller barriers of 0.12 eV, 0.02 eV, and 0.07 eV. The reaction pathway traverses the three transition states as it moves from states A through to D (Figure 3.16). The second transition state (TS2), is particular low (0.02 eV), and may be taken as negligible compared to the TS3 (0.12 eV). The mechanism suggests that energy barrier to dissociate H\textsubscript{2} at the surface FLP site may be lowered by creating opportunities for stable intermediates in the dissociation process. These results are in agreement with the previously suggested idea that the enhanced FLP separation may provide the conditions to create such stable intermediates. Bi has a theoretical atomic radius of 182 pm, whereas the theoretical radius of In is 167 pm. The larger volume occupied by the Bi dopant will induce local changes in strain that will affect the FLP bond separation; however, further investigation is needed. In addition, Bi has a higher ionic potential and electronegativity as compared to In, and these factors are likely more significant to reducing the activation barrier required to dissociate hydrogen compared to the structural effects arising from the larger atomic radius.

3.5 Summary

In the present study, we performed well-tempered Metad-biased AIMD simulations to investigate the mechanism for the RGWS reaction over the In\textsubscript{2}O\textsubscript{3-\textit{x}}(OH)\textsubscript{\textit{y}} surface at temperatures of 20 °C and 180 °C. Free energy surfaces mapping the reaction pathways, transitions states, and locations of energy minima were generated to obtain the energetics for the activation of hydrogen and the capture and reduction of carbon dioxide. Further AIMD results suggest that the surface FLP site is structurally altered under high temperature conditions. In particular, the time-averaged distance between the Lewis acid acting In and the Lewis base acting O on the hydroxyl group was found to increase by 0.04 Å at 180 °C, which may provide conditions required to break the reaction into two smaller energetic steps (Figure 3.5). The reduction of gaseous CO\textsubscript{2} is found to be the rate-limiting step (Figure 3.14), with no significant change resulting from increased temperature conditions; however, the energy barrier corresponding to the adsorption of CO\textsubscript{2} is slightly reduced at 180 °C compared to 20 °C, suggesting that thermal effects may only be relevant to reaction step characterized by adsorptive mechanisms. The dynamics of the
Figure 3.16: Free energy surfaces generated from MetaD-biased AIMD simulations for H$_2$ dissociation over Bi-doped In$_2$O$_{3-x}$(OH)$_y$ at 180 °C. Points A, B, C, and D denote locations of energy minima, and triangles TS1, TS2, and TS3 denote locations of transition states.

product H$_2$O molecule over the In$_2$O$_{3-x}$(OH)$_y$ was also investigated using well-tempered MetaD-biased AIMD. The free energy surface revealed dissociative adsorption of H$_2$O at the In and hydroxyl sites to be preferred over direct desorption from the surface, at both 20 °C and 180 °C. The desorption of H$_2$O was found to have energetic barriers of 1.1 eV and 0.98 eV, at 20 °C and 180 °C, respectively, which strongly suggests that product H$_2$O prevents sustained catalytic activity by blocking surface sites. These results attest to the interesting catalytic mechanisms enabled by of surface FLP chemistry, in particular, the heterogeneous reduction of CO$_2$. 
Chapter 4

Methane Reforming over Ni-Based Bimetallic Catalysts

4.1 Introduction

The steam reforming of methane (SRM) is the largest and most economical way to produce H\(_2\): CH\(_4\) + H\(_2\)O \(\rightarrow\) CO + 3H\(_2\). [68] It is also the primary industrial process to produce syngas, a vital feedstock for the Fischer-Tropsch process. Being highly endothermic, SRM is favoured at high temperatures (\(\sim 900^\circ\)C for Ni-based catalysts. Such high temperatures, however, cause catalytic coking which deteriorates the long-term catalytic activity and hinders the industrial process. Coking occurs because intermediate products lead to the following side reactions to form a more stable form of carbon along the reaction path. [23, 69]

\[
\begin{align*}
2CO & \rightarrow C + CO_2 \quad (4.1) \\
CO + H_2 & \rightarrow C + H_2O \quad (4.2) \\
CH_4 & \rightarrow C + H_2O \quad (4.3) \\
C_{(n)}H_{(2n+2)} & \rightarrow nC + (n+1)H_2 \quad (4.4)
\end{align*}
\]

The long term stability of catalysts used in steam reforming reactions is therefore dictated by their ability to oxidize C atoms while preventing C-C bond formation. There have been significant efforts by the research community over the past forty years to
address these shortfalls. The use of alkali metal promoters integrated into the catalyst structure to neutralize acidic sites and preoccupy the defect sites contributing to carbon formation has been investigated. [69] However, this in turn will concomitantly reduce the reforming rate of methane. Sulfur is also known to impede carbon formation. H$_2$S can selectively block the step and defect sites on a Ni catalyst; but adsorbed Sulfur also poisons the reforming process. [22, 23, 24] Transition metals such as Ru, Rh, Ir, and Pt have been investigated as alternative catalysts for their potential to impede carbon formation under mild reaction conditions [70, 71, 72, 73, 74], but are costly and cannot serve large-scale industrial purposes.

Due to above issues, Ni based bimetallic catalysts have come to the forefront as they offer the possibility of enhancing catalytic performance whilst being more cost-effective. Furthermore, introducing a second transition metal to the conventionally used Ni catalyst enables tuning of the reactivity through the design of specific catalyst structures and compositions. [23, 27, 75] These experimental and theoretical studies have provided understanding of the underlying factors that drive the reaction, which include distribution of particle size, surface geometry, presence of type-specific clustering and relative activation barriers of subsequent steps in methane dehydrogenation. [28, 27, 75, 76] First-principles theoretical studies have been quite useful in understanding both ligand and geometrical effects, not easily isolated in experiments, and can help complement and expedite experimental research which ensemble effects

### 4.2 Literature Review

The introduction of a secondary transition metal (TM) to the Ni-based catalyst has proven to reduce the formation of unwanted carbon products in the SRM and has henceforth uncovered a promising path forward into catalyst optimization for hydrogen production. Combining density functional theory (DFT) with heterogeneous catalyst theory provides an effective method of screening for potential catalyst candidates. DFT offers fundamental insights into the adsorption energies, activation barriers, and the reaction mechanism of the various steps of methane dehydrogenation. Hammer and Norskov’s d-band model has shown the d-band center of TM system to be closely correlated with the TM’s reactivity. [26] Additionally, nudged-elastic-band (NEB) methods and ab-initio molecular dynamics (AIMD) offer insight into activation barriers and the reaction mechanism at finite temperatures. [37] Such theoretically-derived relationships have enabled fast and efficient testing of potential catalysts. Table 4.1 summarizes the literature results from ground-state DFT studies on a variety of bimetallic system The ideal candidate
should demonstrate a low adsorption energy for C* (to prevent coking), as well as a low activation barrier for the rate limiting step of methane dehydrogenation. [23] Expensive metals such as Ru and Pt are not desirable and so Co and Bi are more promising candidates with similar performance. Another challenge for such catalysts, as can be observed from Table 4.1, is the fact that a lower adsorption energy for C* often corresponds to a higher activation barrier for C-H bond breaking. Towards this end, the oxophilicity of Co for oxygen and its preferential binding of O* might present one possible solution as the O* might lower C* adsorption energies and prevent coking. Experimental evidence also points to Ni-Co as an excellent catalyst for the SRM reaction in terms of both activity and stability compared to other Ni-TM combinations [26, 27], and consistently higher catalytic performance compared to monometallic systems [77, 78, 79, 80].

Table 4.1: Literature review of DFT-derived adsorption energies and activation barriers for methane reforming over Ni-based bimetallic catalysts.

<table>
<thead>
<tr>
<th>System</th>
<th>Adsorption Energies (eV)</th>
<th>Activation Energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>CH</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>6.81 [28]</td>
<td>5.11 [28]</td>
</tr>
<tr>
<td></td>
<td>6.78 [81]</td>
<td>6.46 [81]</td>
</tr>
<tr>
<td>Ag/Ni(111)</td>
<td>7.08 [28]</td>
<td>5.31 [28]</td>
</tr>
<tr>
<td>Au/Ni(111)</td>
<td>6.6 [28]</td>
<td>4.95 [28]</td>
</tr>
<tr>
<td>Co/Ni(111)</td>
<td>6.47 [28]</td>
<td>5.06 [28]</td>
</tr>
<tr>
<td>Bi/Ni(111)</td>
<td>6.04 [28]</td>
<td>4.53 [28]</td>
</tr>
<tr>
<td>Pt/Ni(111)</td>
<td>6.47 [82]</td>
<td>6.24 [82]</td>
</tr>
<tr>
<td>Ru/Ni(111)</td>
<td>6.91 [82]</td>
<td>6.62 [82]</td>
</tr>
<tr>
<td>Pd/Ni(111)</td>
<td>6.4 [82]</td>
<td>6.11 [82]</td>
</tr>
<tr>
<td>Sn/Ni(111)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The underlying reason for the increase in C-H bond activation rates has remained unexplained. Experimental research has revealed the need to understand the synergy between the Ni and Co components, since excess Ni content is responsible for carbon formation, whilst excess Co may in turn deactivate the catalyst due to oxidation [23]. A comprehensive DFT study into Co-Ni catalyst system that explains the interplay of electronic and geometrical factors contributing to the activity and stability of the catalyst is currently missing from the literature. The study will address following specific questions:

- What is the role of Co-content on the lattice geometry and its consequence on carbon formation?
- What is the optimal Ni to Co ratio to enhance catalytic activity?
- Which surface sites are the active contributors to catalytic activity?

Currently there are significant gaps between theoretical studies, experimental realities and industrial applications [80], mainly owing to idealizations and approximations used in theoretical modeling. One such challenge is that catalyst nano-particles in experimental studies have an average size of 5-20 nm, currently inaccessible to computational modeling, and various surface effects such as facets, dangling bonds, defects and kinks. We therefore propose a comprehensive theoretical study that probes the structure and dynamics of the Co-Ni bimetallic DFT based computational tools, including temperature-driven and excited-state studies, in order to provide a complete mechanistic interpretation of C-H bond activation as described below.

### 4.3 Computational Details

#### 4.3.1 Methods

All structure and energy calculations were performed via periodic plane-wave DFT using the Vienna ab initio simulation package (VASP). A 64-atom, 444 supercell with a 20 Å vacuum was used to model the Ni(111), Co(111), and Ni-Co(111) surfaces. The (111) surface was chosen given is it the most thermodynamically stable surface of the face-centered cubic (FCC) crystallographic structure, which is characteristic of Ni and Co, the latter which undergoes a phase transition from hexagonal close-packed (HCP) to fcc at temperatures above 695 K [83]. Computations were implemented using the Perdew-Burke-Emzerh of (PBE) exchange correlation functional [65], together with the Projector Augmented-Wave (PAW) method-derived pseudopotentials [31, 30]. Kinetic energy cutoffs and the self-consistent field convergence criterion were set to 400 eV and 10^-4 eV, respectively. Brillouin zone integrations were performed with 441 Monkhorst-Pack k-point mesh [84]. Wave function occupancies were determined using second-order Methfessel-Paxton smearing over a width of 0.2 eV. All calculations were spin-polarized to account for the magnetic properties of Ni and Co. Within the four-layer slab, the atoms from the bottom two layers were frozen in all calculations, while the atoms from the top two layers, gas phase species, and adsorbed species were allowed to relax. Relaxation was performed using the conjugate gradient minimization algorithm until the energy difference between ionic steps was 1 X 10^{-3} eV. Adsorption energy was calculated by
\[ E_{\text{adsorption}} = E_{\text{adsorbate/surface}} - (E_{\text{adsorbate}} + nE_{\text{surface}}) \]  

where \( E_{\text{adsorbate/surface}} \) is the total energy of the surface with adsorbed species, \( E_{\text{adsorbate}} \) is the total energy of the free adsorbate, and \( E_{\text{surface}} \) is the total energy of the bare surface. By this definition negative values of adsorption energy indicate exothermic adsorption. Transition states and activation barriers along a minimum energy reaction path were determined using the climbing image nudged elastic-band (CI-NEB) method [33] with ten images. Bader charge analysis [44, 42] was used to obtain an approximation of the relative charges associated with individual atoms at the reactant state, transition state, and product state for C-H activation over the Ni(111), O*-covered Co(111), and O*-covered Ni-Co(111).

### 4.3.2 Models

To develop a model to study the bimetallic Ni-Co catalyst surface, we investigated the effect of Co clustering at the surface by computing the cohesive energies of 6 surfaces that were randomly generated using MATLAB. The bottom two layers of each model were composed uniquely of nickel atoms that were frozen, while the top two contained a 3:1 Ni:Co ratio with atoms free to move. The structures were relaxed to their minimum energy using DFT, and no significant change in cohesive energy was found among the different structures samples. For this reason, we chose to the Ni-Co(111) surface, consisting of a 1:1 ratio of Ni to Co atoms, with alternating rows of Ni and Co atoms in the top two layers of the model. The adsorption of oxygen was calculated at all possible sites of the (111) surface, and was found be to be greatest at HCP sites, compared to top sites and FCC sites, for both Ni (-523 kJ mol\(^{-1}\)) and Co (-555 kJ mol\(^{-1}\)). Given these findings, 0.75 ML O* covered Co(111) and Ni-Co(111) models were generated with oxygen bound to HCP sites, as shown in Figure 4.1.

The reaction of was first modelled on a Ni(111) surface, to serve as a reference to which we could compare our results to the vast body of scientific literature existing on nickel catalysts for methane reforming. Our results for the adsorption of CH\(_3\) to various sites, as well the computated activation barrier, agree favorably with previously reported results (Figure 4.2) that show CH\(_3\) to bind most favourable to 3-fold FCC sites. They results validate our selected parameters, which were therefore used in subsequent simulations. To develop a model to study the bimetallic Ni-Co catalyst surface, we investigated the effect of Co clustering at the surface by computing the cohesive energies of 6 surfaces that were randomly generated using MATLAB. The bottom two layers of each model were
composed uniquely of nickel atoms that were frozen, while the top two contained a 2:1 Ni:Co ratio with atoms free to move. The structures were relaxed to their minimum energy using DFT, and no significant change in cohesive energy was found among the different structures samples. For this reason, we chose to study straightforward Ni-Co(111), with alternating rows of Ni and Co atoms in the top two layers of the model.

Table 4.2: Comparison of \( \text{CH}_3 \) binding energy at Top, HCP, and FCC surface sites with previous results

<table>
<thead>
<tr>
<th>Site</th>
<th>Ho et al., 2013 [85]</th>
<th>Present study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>-1.72 eV</td>
<td>-2.21 eV</td>
</tr>
<tr>
<td>HCP</td>
<td>-1.97 eV</td>
<td>-2.51 eV</td>
</tr>
<tr>
<td>FCC</td>
<td>-2.01 eV</td>
<td>-2.56 eV</td>
</tr>
</tbody>
</table>

### 4.4 Results and Discussion

#### 4.4.1 \( \text{CH}_3 \) Adsorption Energy

In order to compute the activation barrier of the \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \) reaction, we first determined the most favourable surface site to which \( \text{CH}_3 \) may bind. To do this, we calculated the adsorption energy of \( \text{CH}_3 \) to the Top, HCP, and FCC sites on Co(111), as shown in Table 4.3. In both cases, \( \text{CH}_3 \) is found to bind most readily to the 3-fold FCC site, with a preference to an Ni over a Co site. These findings are later considered when setting up more sophisticated models that simultaneously involve Ni and Co atoms at the surface.
Table 4.3: Binding energy of \( \text{CH}_3 \) at Top, HCP, and FCC sites on select (111) surfaces

<table>
<thead>
<tr>
<th>System</th>
<th>Top</th>
<th>HCP</th>
<th>FCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)</td>
<td>-2.21 eV</td>
<td>-2.51 eV</td>
<td>-2.56 eV</td>
</tr>
<tr>
<td>Co(111)</td>
<td>-1.45 eV</td>
<td>-1.98 eV</td>
<td>-2.02 eV</td>
</tr>
</tbody>
</table>

4.4.2 \( \text{O*} \) Adsorption Energy

Given that we expect chemisorbed \( \text{O*} \) to play a role in the reaction mechanism, we tested the binding energy of \( \text{O*} \) at various Ni and Co site combinations (see Table 4.5). We expect weakly bound \( \text{O*} \) to enhance catalytic activity by possessing a greater propensity to attract a hydrogen atom on the incoming methane molecule. For this reason, we are interested in finding the optimal concentration of chemisorbed \( \text{O*} \) on the surface that result in sufficiently weakened metal-\( \text{O*} \) bonds such that the \( \text{O*} \) will more readily activate the C-H bond of \( \text{CH}_4 \). Table 4.4 shows binding energies of a single \( \text{O*} \) to the two possible 3-fold sites on Ni(111) and Co(111). \( \text{O*} \) is found to be most weakly adsorbed to the HCP site on Ni-Ni-Ni. Next, we generated two NiCo(111) surfaces, containing a 1:1 ratio of Ni to Co atoms, with 0.75 ML \( \text{O*} \)-coverage to model the most promising structures found from kinetic experiments. Given our results showing \( \text{O*} \) to be more weakly bound to HCP sites, we computed the binding energy of every different type of 3-fold site (ie. Ni-Ni-Co, Ni-Co-Co, and Co-Co-Co) to understand the effect of neighbouring vacant \( \text{O*} \) sites on the adsorption energy of \( \text{O*} \) at a given site. Results from these studies are shown in Table 4.5 and with site locations shown in Figure 4.2. A more illustrative view of the trends is depicted in graph shown in Figure 4.3. Interestingly, the trend reveals that \( \text{O*} \) is not necessarily more strongly bound when fewer neighbouring \( \text{O*} \) are present. For each site type, the \( \text{O*} \) is most weakly bound when it is surrounded by 5 adsorbed \( \text{O*} \) and one vacant site. When an additional neighbouring \( \text{O*} \) is removed (to produce 4 neighbouring \( \text{O*} \) and 2 vacant sites), \( \text{O*} \) becomes more strongly bound, and even more so if the vacant sites are sitting adjacent to eachother, forming a vacant site pair. We assume it is not realistic for our model to contain an overly \( \text{O*} \)-saturated surface, as a reasonable area of metal atoms should be exposed to reliably interact with the methane molecule. Therefore, we neglect the sites with only 0, 1, or 2 non-adjacent neighbouring \( \text{O*} \) vacancies, and only consider those with either 2 adjacent or 3 neighbouring vacant \( \text{O*} \) sites. Of these, the Ni-Ni-Co site with 2 adjacent neighbouring vacant \( \text{O*} \) sites is found to produce the most weakly bound \( \text{O*} \), making this the configuration of choice for our subsequent studies of the reaction pathway.
Table 4.4: Binding energy of a single O* on Ni(111) and Co(111)

<table>
<thead>
<tr>
<th>FCC site</th>
<th></th>
<th>HCP site</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Ni-Ni</td>
<td>-5.54 eV</td>
<td>Co-Co-Co</td>
<td>-5.66 eV</td>
</tr>
<tr>
<td></td>
<td>-5.42 eV</td>
<td></td>
<td>-5.75 eV</td>
</tr>
</tbody>
</table>

Table 4.5: Binding energy of O* at different HCP sites on 0.75 ML O* Ni-Co(111) and Co(111)

<table>
<thead>
<tr>
<th>Site</th>
<th>Type</th>
<th>Number of surrounding vacant O* sites</th>
<th>Number of surrounding pairs of vacant O* sites</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ni-Co-Co</td>
<td>0</td>
<td>0</td>
<td>-4.16</td>
</tr>
<tr>
<td>B</td>
<td>Ni-Co-Co</td>
<td>3</td>
<td>1</td>
<td>-3.93</td>
</tr>
<tr>
<td>C</td>
<td>Ni-Ni-Co</td>
<td>2</td>
<td>0</td>
<td>-3.65</td>
</tr>
<tr>
<td>D</td>
<td>Ni-Co-Co</td>
<td>1</td>
<td>0</td>
<td>-3.95</td>
</tr>
<tr>
<td>E</td>
<td>Ni-Co-Co</td>
<td>2</td>
<td>1</td>
<td>-4.28</td>
</tr>
<tr>
<td>F</td>
<td>Ni-Ni-Co</td>
<td>0</td>
<td>0</td>
<td>-3.58</td>
</tr>
<tr>
<td>G</td>
<td>Ni-Ni-Co</td>
<td>3</td>
<td>1</td>
<td>-3.88</td>
</tr>
<tr>
<td>H</td>
<td>Ni-Co-Co</td>
<td>2</td>
<td>0</td>
<td>-3.87</td>
</tr>
<tr>
<td>I</td>
<td>Ni-Co-Co</td>
<td>1</td>
<td>0</td>
<td>-3.49</td>
</tr>
<tr>
<td>J</td>
<td>Ni-Ni-Co</td>
<td>2</td>
<td>1</td>
<td>-3.84</td>
</tr>
<tr>
<td>K</td>
<td>Co-Co-Co</td>
<td>0</td>
<td>0</td>
<td>-4.40</td>
</tr>
<tr>
<td>L</td>
<td>Co-Co-Co</td>
<td>3</td>
<td>1</td>
<td>-4.50</td>
</tr>
<tr>
<td>M</td>
<td>Co-Co-Co</td>
<td>2</td>
<td>0</td>
<td>-4.31</td>
</tr>
<tr>
<td>N</td>
<td>Co-Co-Co</td>
<td>1</td>
<td>0</td>
<td>-4.25</td>
</tr>
<tr>
<td>O</td>
<td>Co-Co-Co</td>
<td>2</td>
<td>1</td>
<td>-4.56</td>
</tr>
</tbody>
</table>

Figure 4.2: Locations of HCP sites on NiCo(111) and Co(111) surfaces corresponding to those listed in Table 4.5. O atoms are shown in red, Ni atoms are shown in blue, and Co atoms are shown in green.
Figure 4.3: Trends in individual oxygen binding energy at Ni-Ni-Co, Ni-Co-Co, and Co-Co-Co sites as a function of the number of vacant neighbouring oxygen sites.

### 4.4.3 Reaction Pathways and Activation Barriers

Reaction pathways were investigated first using the Nudged-Elastic-Band (NEB) and then by using the Climbing Image Nudged-Elastic-Band (CI-NEB) method to obtain the activation barriers and transition state structures for the $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ reaction over selected surfaces. To set up the these force-biased simulations, the reactant and product states were first modelled with the $\text{CH}_3$ and $\text{H}$ product moities and chemisorbed $\text{O}^*$ placed at the optimized sites as determined by the adsorption energy studies, and were subsequently relaxed to their minimum energy configuration. The resulting reaction pathways at the selected surfaces are shown in Figure 4.4.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Length of C-H bond at transition state (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(111)</td>
<td>1.62</td>
</tr>
<tr>
<td>Ni(111) with 1 substituted Co</td>
<td>1.73</td>
</tr>
<tr>
<td>Ni(111) with 1 substituted Co and 1 surface O*</td>
<td>1.45</td>
</tr>
<tr>
<td>NiCo(111) with 1:1 Ni:Co ratio</td>
<td>1.62</td>
</tr>
</tbody>
</table>

DFT calculations show evidence for the existence of different types of active site pairs in the presence of a secondary metal and varying concentrations of chemisorbed $\text{O}$; in particular, $\text{O}$ species adsorb most readily to Co-Co-Co sites (-527 kJ mol$^{-1}$), compared to Ni-Co-Co sites (-413 kJ mol$^{-1}$) and Ni-Ni-Co sites (-371 kJ mol$^{-1}$). The adsorption of
Figure 4.4: Reaction pathway curves, along with activation energies ($E_a$) and reaction energies ($E_{rxn}$), generated from NEB and CI-NEB simulations for the $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ reactions over select surfaces. The images corresponding to the reactant, transition, and product states are shown below each NEB curve. Blue represents Ni atoms, yellow represents C atoms, cyan represents H atoms, green represents Co atoms, and red represents O atoms.
O* to the bimetallic surface is not only dependent on the metal(s) that form the site, but also on the number and distribution of neighbouring adsorbed O* species; in particular, O* is most weakly bound at sites containing 5 neighbouring chemisorbed O*, and the O* becomes more strongly bound with each removal of a neighbouring adsorbed O* species. The thermodynamic stability of metal-O* active site pairs on the surface, as shown by the ground-state DFT calculations, strongly suggests catalytic involvement of adsorbed oxygen species on the Co(111) and Ni-Co(111) surfaces.

From these reaction pathways we can obtain the activation energy barrier, the energy of reaction, as well as the structure of the transition state. The latter, in addition to a bader charge analysis, may be used to predict the electronic nature of the C-H activation mechanism. The activation energies are directly related to the reaction rates by the Arrhenius equation and therefore such information is of critical importance in estimating the ensuing reaction rates. Still, we must consider that while these results hold significant predictive power, they are based solely on reaction energetics, and not kinetics. While Ni(111) clearly possesses the lowest activation barrier, the reaction rate over Ni(111) is susceptible to decreasing over time due to catalytic coking, whereas catalysts containing Co are less likely to form unwanted carbon products and therefore more robust over time. While we have yet to investigate the formation of carbon products at these surfaces, our results provide insight into the interplay between Ni, Co, and chemisorbed O* on the reaction mechanism. The reactant, transition state, and product structures for the reaction over Ni(111), Co(111) with 0.75 ML O* coverage, and Ni-Co(111) with 0.75 ML O* coverage are shown in Figures 4.8, 4.9, and 4.10, respectively.

The similarity of the transition state to the product state is indicative of the nature of the C-H activation; that is, whether it is occurring via sigma bond metathesis in which the metal and oxygen work synergistically as an active site pair and polarize the C-H bond via a four-centre transition state or alternatively, oxidative addition where the activation proceeds via a change in oxidation state of the active metal site. Sigma bond metathesis is generally a more effective mechanism to activate a C-H bond. We determine nature of the mechanism by a variety of indicators. In the case of sigma bond metathesis, transition states are expected to occur earlier along the reaction path, and C-H bond lengths at the transition state are expected to be shorter compared to reactions over transition metal surfaces which typically occur via oxidative addition. A summary of computed C-H bond lengths at the transition state are listed in Table 4.6. Indeed, the systems containing O* (Ni(111) with 1 substituted Co and 1 surface O* and Ni-Co(111) with 0.75 ML O* coverage) possess shorter C-H bond lengths at their transition states. Additionally, transition states for these systems occur slightly earlier along the reaction
pathway as compared to the systems void of O*, indicating that the reaction is proceeding via the more effective sigma bond metathesis pathway when chemisorbed O* is present.

Figure 4.5: Reactant state, transition state, and product state for CH$_4$ → CH$_3$ + H over Ni(111); light blue atoms denote Ni, green atoms denote C, and dark blue atoms denote H.

Figure 4.6: Reactant state, transition state, and product state for CH$_4$ → CH$_3$ + H over Co(111) with 0.75 ML O* coverage; purple atoms denote Co, green atoms denote C, and dark blue atoms denote H.

4.5 Summary

While the DFT methods used here allow us to probe the atomic interactions between the methane and the catalyst surface and provide insight in the reaction mechanism,
Figure 4.7: Reactant state, transition state, and product state for \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \) over Ni-Co(111) with 0.75 ML O* coverage; light blue atoms denote Ni, purple atoms denote Co, green atoms denote C, and dark blue atoms denote H.

Figure 4.8: Reaction pathway curves generated from NEB and CI-NEB simulations for the \( \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \) reactions over Ni(111).
Figure 4.9: Reaction pathway curves generated from NEB and CI-NEB simulations for the $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ reactions over 0.75 ML O*-covered Co(111).

Figure 4.10: Reaction pathway curves generated from NEB and CI-NEB simulations for the $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ reactions over 0.75 ML O*-covered NiCo(111).
otherwise impossible via experiment alone, we encountered certain challenges setting up a reliable DFT model. The computationally-expensive nature of these calculations means that the our calculations may not converge within reasonable time limits should the simulation not be carefully optimized. In particular, we encountered difficulties when introducing the cobalt pseudopotential; that is, the rate of convergence in all DFT calculations was significantly slower to that of the Ni systems. We are still encountering difficulties in producing reliable calculations to probe the Co(111) surface with 0.75 ML O* coverage.

- CH$_3$ binds most readily to FCC sites, compared to HCP and Top sites
- Ni-Ni-Co 3-fold HCP sites are the optimal sites to produce weakly-adsorbed surface O* species
- The presence Co increases the activation barrier of the CH$_4$ $\rightarrow$ CH$_3$ + H reaction
- The presence of O* is likely enabling the reaction to proceed via the more effective sigma bond metathesis pathway, rather than via oxidative addition.
Chapter 5

Conclusion and Future Work

5.1 Summary and Overall Contribution

In order to address the world’s urgent need for a reliable alternative to fossil fuel sources, whilst still considering the inevitable time required to shift the global energy economy away from current non-sustainable practices, the investigation here presented was conducted with two principal objectives in mind: (1) to study catalyst materials capable of reducing CO$_2$ into sustainable carbon-based fuels, and (2) to study enhanced Ni-based catalysts to improve the efficiency the industrially-ubiquitous methane reforming reaction. Metal oxides are a class of materials with unique electronic and chemical properties that have been demonstrated to serve as excellent electrochemical, thermochemical, and photochemical catalysts. Gas-phase heterogeneous catalysis over metal oxides was investigated, as gas-phase systems are more robust and practical to implement at an industrial level, as compared to homogeneous catalytic systems which require the initial sequestration of any gas-phase reactants into aqueous solution. DFT was used to obtain energies associated to the adsorption of gas-phase adsorbates on the metal oxide surfaces. Additional DFT-based methods, such as NEB and MetaD-biased AIMD were used to study the reaction mechanisms ensuing on the catalyst surfaces. The reduction of carbon dioxide and first step of the methane reforming reaction were studied using DFT in conjunction with MetaD-biased AIMD and NEB, respectively, to obtain the reaction pathways, transition state structures, and activation barriers associated with the reactions. The main contributions and conclusions drawn from these studies are described below:
1. Investigating the reduction of CO\(_2\) over In\(_2\)O\(_{3-x}\)(OH)\(_y\)

- An increase in temperature from to 20 °C to 180 °C effectively reduces the activation barriers associated with the adsorptive processes of the RWGS reaction over hydroxylated indium oxide nanoparticles.

- Product water molecules act as inhibitors on the surface of In\(_2\)O\(_{3-x}\)(OH)\(_y\), preventing sustained catalytic activity.

- The structure of Frustrated Lewis Pair on the catalyst surface, in particular, the length of the Lewis acid-base bond, may influence the reactivity of the site and its ability to activate gaseous molecular hydrogen.

2. Investigating methane reforming over bimetallic catalysts

- The introduction of cobalt to nickel-based catalysts increases the energy barrier required for the first C-H bond activation in the SRM reaction.

- Chemisorbed oxygen provides the conditions for an alternate, more efficient methane activation mechanism to proceed over NiCo surfaces.

- Ni-Ni-Co 3-fold HCP sites are the optimal sites to produce weakly-bound surface O-species.

- More concentrated oxygen monolayers reduce the adsorption energy of individual oxygen atoms, creating weakly bound oxygen sites which may alter the mechanism for C-H activation over Ni-Co surfaces.

5.2 Future Work

There remains many issues to be addressed before a complete understanding of the interplay between electronic, structural, and catalytic properties of metal oxide surfaces can be reached. Still, they continue to be demonstrated, both computationally and experimentally, as excellent candidates to reduce carbon-based compounds, both photochemically and thermochemically. The present work focused on computationally investigating In\(_2\)O\(_{3-x}\)(OH)\(_y\) and oxygenated NiCo surfaces catalysts for reducing CO\(_2\) and reforming CH\(_4\), respectively. While a computational approach to investigating catalytic mechanisms over surfaces can offer insights that are otherwise unavailable experimentally,
future studies would benefit from further combined rigorous computational and experimental investigations. Given the results here presented, research to further advance in this direction should involve the following for each catalytic system:

1. **Investigating the reduction of CO$_2$ over In$_2$O$_{3-x}$(OH)$_y$**
   - Study the effect of changes to the surface Frustrated Lewis Pair structure on its reactivity; in particular, identify the optimal electronic and structural conditions needed to enhance their ability to activate H$_2$.
   - Study the effect of doping In$_2$O$_{3-x}$(OH)$_y$ nanoparticles with other transition state metals (ie. Bi, Sb, Al) at both the Lewis acid and Lewis base surface sites in order to further reduce activation barriers and prevent catalytic activity loss over time.
   - Study the effect of increased defect concentrations (O-vacancies, surface-bound hydroxyl groups) on the indium oxide system to the surface reactivity.
   - Continue exploring CO$_2$ reduction pathways on other material systems using combined experimental and computational investigations.

2. **Investigating methane reforming over bimetallic catalysts**
   - Determine the most stable stoichiometry and configuration of different secondary metals on Ni-based bimetallic systems.
   - Study C-H activation mechanism over bimetallic catalyst systems under finite-temperature conditions via MetaD-biased AIMD.
   - Study the consequences of structural defects (kinks, edges) on C-H activation over Ni-based bimetallic catalysts.
   - Obtain a more reliable Ni-based bimetallic surface model using alternative computational approaches, such as Monte Carlo techniques.
Bibliography


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