Catalytic Conversion of Carbon-Containing Compounds into Valuable Chemicals and Fuels

Zhuo Cheng
Washington University in St. Louis

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Catalytic Conversion of Carbon-Containing Compounds into Valuable Chemicals and Fuels

by

Zhuo Cheng

A dissertation presented to the Graduate School of Arts and Sciences of Washington University in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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Zhuo Cheng

Washington University in Saint Louis
August 2014
Dedicated to my parents.
Conversion of carbon-containing compounds, especially C1 compounds such as carbon dioxide and methane, to valuable chemicals and fuels will hopefully address concerns over decreasing supplies of fossil fuels and mitigate the effects of greenhouse gas emissions on global climate change. Many challenges, however, remain to be addressed before these technologies may be adopted on an industrial scale. Chiefly, catalysts must be developed to activate carbon-containing compounds from their thermodynamically stable ground states, using hydrogen, electrons, or heat as energy sources. We chose as model catalytic systems: 1) Metathesis of ethene and 2-butene; 2) Methane dehydrogenation and carbon dioxide hydrogenation.

We developed three computational methodologies to study these processes across a range of length and time scales. First, we investigated how electronic structure affects the properties and reactivity of these catalyst systems; by computing the partial electronic density of states, electronic localization function, and excess spin density, we showed how redox supports, such as ceria, promote electron transfer reactions. We applied this to the studies of...
methane activation and carbon dioxide activation. Second, we developed a non-equilibrium thermodynamics approach to calculate energies of activation at finite temperatures, based on the Bronsted-Evans-Polanyi principle and the Nudged Elastic Band method. Third, we developed an approach to numerically compute heat capacities and other thermodynamic properties on extended catalytic systems that are comparable in accuracy and precision to methods that have been well-developed for gas-phase molecules. We applied these to the studies of metathesis propagation and carbon dioxide hydrogenation.

We gained mechanistic, thermodynamic, and kinetic insight into the elementary steps that comprise larger reaction networks of interest to the broader catalysis community. Ultimately, these theoretical and computational predictions can be used to guide experimental design, synthesis, and characterization of new catalyst systems.
Chapter 1

Introduction

Propene is one of the most important starting products in the petrochemical industry, being the raw material for a wide variety of commodity chemicals ranging from plastic products to gasoline components [1]. In the year 2008 the worldwide sales of propene reached a value of over 90 billion US dollars. In the rapidly developing global economy, the demand for basic organic materials produced with propene as their raw material is projected to increase by more than 20 million tons by 2020 [2] as shown in Figure 1.1. Thus, we aim to discover efficient and high-yield routes to produce propene.

![Figure 1.1: Polypropene world supply/demand forecast](image)

The main route for producing propene commercially is steam cracking of hydrocarbons, which dates back to the 1950’s. The saturated hydrocarbon feedstock, including ethane, propane, natural gas, and liquid petroleum, are diluted with steam and cracked in pyrolysis.
furnaces. These cracked gases and then distilled to remove hydrogen, methane and ethane while separating out acetylene and propene. The typical operating conditions of the ethane steam cracker are temperature between 750-800 °C, pressure between 1-1.2 atm, and steam-to-ethane ratio of 0.5. Liquid feeds are usually cracked with lower residence times and higher steam dilution ratios compared to gaseous feeds. Unfortunately, a substantial amount of energy is required to facilitate the steam cracking process for olefin production. Since the reaction is strongly endothermic it is favored at high temperatures and low pressures. Superheated steam is essential to reduce the partial pressure of the reacting hydrocarbons and reduce carbon deposits that are formed by the pyrolysis of hydrocarbons at high temperatures [3, 4].

Another major commercial source of propene is refinery fluid catalytic cracking (FCC). The main FCC sections consist of the feed injection system, stripper, riser, fractionator and regenerator. A fluidized system needs to be used to drive the catalyst and transfer heat between the reactor and the regenerator. Cracking reactions are endothermic and the combustion of catalyst-deposited coke in the regenerator provides the necessary heat. To achieve higher yields of propene, the hydrogen content of the feedstock must be high and the sulfur content must be low. This can be achieved by utilizing low sulfur crude oils or a higher performance feed hydrotreaters upstream from the FCC unit. Currently, there are several commercial FCC processes being employed, with the major differences in the method of catalyst handling [5, 6]. However, it is not ultimately economical to build an FCC due to their low yields for propene production.

The third main route for commercial propene production is propane dehydrogenation, which is again a highly endothermic reaction. A relatively high conversion of propane can be achieved at high temperatures and low pressures. For propane dehydrogenation, at least two fluidized-bed reactors must be used so that the catalyst in one reactor can be regenerated while the process continues without interruption in the second reactor. Thus the main disadvantage is that a separate regeneration unit is required. The other disadvantage of this route is the preponderance of side reactions that occur simultaneously with the main reaction. The side reactions lead to the formation of light and heavy hydrocarbons which ultimately result in the deposition of coke on the catalyst [7]. Considering these drawbacks of traditional processing routes, economical and environmentally friendly routes for propene production should be studied and developed.
Olefin metathesis is an organic reaction that entails the redistribution of fragments of alkenes (olefins) by the scission and regeneration of carbon-carbon double bonds [8]. Catalysts for this reaction have evolved rapidly for the past few decades. Compared to the traditional high temperature/pressure steam cracking and FCC method, olefin metathesis routes promoted by heterogeneous catalysts rely less on large sources of heat [9] and are carbon neutral. Generally, heterogeneous catalysts containing Re, Mo, or W [10, 11, 12, 13, 14] are favored over homogeneous catalysts for metathesis reactions due to their ease of separation, stability, and recyclability [15]. Thus, olefin metathesis processes, which are solvent-free, generate little waste, and require low catalyst loads, are inherently energy-efficient and cost-effective.

Tungsten trioxide WO$_3$ is well-known for its stability over industrial reaction temperature ranges, and it also can be easily deposited on supports using physical or chemical approaches [16, 17, 18, 12]. Several researchers explored the use of alumina- or silica-supported WO$_3$ as a catalyst for metathesis between ethene and trans-2-butene. Chen et al. [19] found that the working lifetime of the WO$_3$ catalyst decreases with the weight hourly space velocity during metathesis reactions, which thus presents a useful guideline for engineering metathesis processes. Davazoglou et al. [20] obtained equal metathesis activity with well-dispersed, low loading WO$_3$/SiO$_2$ catalysts, compared to catalysts of higher tungsten content. Huang et al. [21, 22] prepared a series of WO$_3$ catalysts by the thermal spread method and found that proportional correlation between the concentration of tetrahedral tungsten oxide species and catalytic activity for metathesis. While W is octahedrally coordinated in all solid WO$_3$ phases, such as the orthorhombic, monoclinic, and triclinic phases, it can assume a distorted octahedral coordination upon WO$_3$ deposition [23], or even tetrahedral coordination if the loading is small enough for W to interact directly with the support [24]. Liu et al. [25] deposited WO$_3$ on alumina supports, and showed that a moist atmosphere hastened the calcination of the catalyst to expose surface facets. Chaemchuen et al. obtained Raman, UV-Vis and H$_2$-TPR spectra that suggest WO$_3$ catalysts calcined at 550 °C exhibit high activity for the metathesis of ethene and trans-2-butene to produce propene [26]. Thus, the prospects for industrial-scale propene production via metathesis over supported WO$_3$ appear to be quite promising.

Another idea is utilization of the greenhouse gas methane and carbon dioxide to produce propene. It is well known that propene can be produced by the MTO Process (Methanol to Olefin) and methanol can be obtained by CO$_2$ hydrogenation. Thus, it is very significant to
develop an effective catalytic route to take hydrogen atoms from CH\textsubscript{4} for CO\textsubscript{2} hydrogenation. Because the mitigation of carbon dioxide levels in the atmosphere would slow down global climate change, this route shows great potential and is valuable for environmentally friendly propene production. It is widely believed that the key step in CO\textsubscript{2} utilization is the activation of the C=O bond and charge transfer for the eventual formation of an anion radical species [27]. Since CO\textsubscript{2} is thermodynamically stable and the formation of the radical is difficult in the gas phase [28] (i.e., -1.90 V vs. NHE [29]), we need to find appropriate catalysts for lowering the activation barrier to (photo)electrochemical CO\textsubscript{2} reduction. There have been several metal oxides proposed for CO\textsubscript{2} activation, such as ZrO\textsubscript{2} [30], TiO\textsubscript{2} [31, 32, 33, 34], MgO [35], and CaO [36]. Among these various catalysts for CO\textsubscript{2} activation, ceria (CeO\textsubscript{2}) is attracting increased interest due to its high oxygen storage capacity. Ceria is commonly used for oxidation and reduction reactions, since Ce ably and reversibly converts between Ce\textsuperscript{4+} and Ce\textsuperscript{3+} upon release and storage of oxygen [37].

Based on these ideas and concerns, we try to explore the catalytic conversion of these carbon-containing compounds to provide fundamental insights on chemical reactions and catalyst design for propene production. Although a number of experimental studies have already done on metathesis and CO\textsubscript{2} hydrogenation, many questions about these catalytic reactions have not been answered, such as: 1. What are the active sites of these catalysts? 2. What is the reaction mechanism? 3. What is the structure/activity relationship? It is difficult to get clear answers by experimental work alone due to the cost and current limitations on spectroscopic techniques.

In this research thesis the catalytic transformations of carbon-containing compounds into valuable chemicals are investigated by first-principles calculations based on density functional theory (DFT). DFT is a computational quantum mechanical modeling method that calculates the electronic structure of many-body systems by solving the Schrödinger equation. The ground state of a system is its lowest-energy state, and the energy of the ground state is known as the zero-point energy of the system. The Schrödinger equation is a partial differential equation that describes the behavior of the quantum state of a physical system. In its time-independent, non-relativistic form it is given as:

\begin{equation}
\hat{H}\Psi(r_i, R_j) = E\Psi(r_i, R_j)
\end{equation}
where $\hat{H}$ is the many-body Hamilton operator providing the total energy $E$ of the system, and $\Psi(r_i, R_j)$ is the many-body wavefunction that depends on the nuclear positions $R_j$ and the electron coordinates $r_i$ [38]. The Hamiltonian itself has three main contributions: The kinetic energy operators $\hat{T}$ of the nuclei and the electrons, the interaction with the external potential which is the interaction of electrons with the nuclei $\hat{V}$, and the electron-electron interaction $\hat{U}$ [39].

$$\hat{H} = \hat{T} + \hat{V} + \hat{U} \quad (1.2)$$

There are three spatial coordinates for each electron and for each nucleus, so for a system consisting of $N$ electrons and $M$ nuclei there are $3(N + M)$ degrees of freedom. Due to the large number of variables on which the many-body wavefunction $\Psi(r_i, R_j)$ depends, solving Eq. (1.1) is difficult. Born and Oppenheimer achieved a first simplification by taking into account the large mass difference between the electrons and the nuclei. The electrons move much faster than the nuclei so that positions of the nuclei can be assumed to be static. In this case the motion of the electrons is separated from the motion of the nuclei. The kinetic energy of the nuclei can be set to zero and the nuclear-nuclear repulsion is a constant. It is known as Born-Oppenheimer approximation [40]. Even though the number of degrees of freedom is reduced to $3N$ by the Born-Oppenheimer approximation, the remaining electronic many-body problem is still hard to be solved exactly, except for the simplest system like a free hydrogen atom or one-electron ions. The electron density was used for the first time to calculate the total energy of a system by Thomas and Fermi in the late 1920’s [41, 42]. The electron density $n$ corresponding to a normalized $N$-electron wavefunction is defined as:

$$n(r) = N \int \cdots \int |\Psi(r_1, r_2, \ldots, r_N)|^2 dr_2 \cdots dr_N \quad (1.3)$$

where $r$ denotes the spatial coordinates of the density. The application of electron density further reduces the number of degrees of freedom from $3N$ to 3 coordinates. The energy is minimized with respect to the electron density to obtain the ground state energy of the system. However, the results were not very satisfying due to the neglected exchange and correlation in the Thomas-Fermi model.
DFT was established as a theory in 1964 by Hohenberg and Kohn who showed that the external potential $V_{\text{ext}}$ is a unique functional of the electron density $n$ [39]. Then it was developed by the introduction of a non-interacting reference system by Kohn and Sham [43]. The Kohn-Sham orbitals $\phi_i$ are determined to generate the density of the fully interacting many-body system in a self-consistent way from the Kohn-Sham equations shown as below:

$$(-\frac{\hbar^2}{2m} \nabla^2 + \nu_{\text{eff}})\phi_i(r) = \epsilon_i \phi_i(r)$$  \hspace{2cm} (1.4)

where $\epsilon_i$ denotes the orbital energy of the corresponding Kohn-Sham orbital $\phi_i(r)$, and the $\nu_{\text{eff}}$ is called as the Kohn-Sham potential. The density for the real system is obtained as the density of this non-interacting orbital system:

$$n(r) = 2 \sum_{i}^{N} |\phi_i(r)|^2$$  \hspace{2cm} (1.5)

To be able to apply the Kohn-Sham equation above one needs an explicit expression for the exchange correlation energy $E_{xc}$. The simplest approximation of the exchange correlation energy is the local density approximation (LDA) based on the homogeneous electron gas proposed also by Kohn and Sham [43]. $E_{xc}(n)$ is a uniform electron distribution on a positive background charge distribution for overall charge neutrality. It assumes that exchange and correlation depend only on the local value of the density. Thus, $E_{xc}[n(r)]$ at position $r$ is identical to $E_{xc}^{LDA}[n(r)]$ of the homogeneous electron gas with the same density. The exchange-correlation functional can then given by:

$$E_{xc}^{LDA}[n(r)] = \int n(r)\epsilon_{xc}[n(r)]dr$$  \hspace{2cm} (1.6)

where $\epsilon_{xc}[n(r)]$ is the exchange-correlation energy per particle of the homogeneous electron gas. $E_{xc}^{LDA}[n(r)]$ can be split up into the exchange contribution $E_{x}^{LDA}[n(r)]$ and the correlation contribution $E_{c}^{LDA}[n(r)]$. The exchange term can be obtained analytically in case of the homogeneous electron gas while the correlation energy can be numerically known from quantum Monte Carlo calculations [44]. Although the LDA is an unrealistic model, it was widely used as the standard functional until the 1990’s with often better results than
Hartree-Fock mean-field approximation for many systems. However, the LDA typically overestimates binding energies and underestimates bond lengths; thus the results using the LDA are not accurate for systems with less homogeneous electron densities. The LDA expression for the exchange correlation energy is improved by introducing a dependence on the gradient of the electron density [45]. The $E_{xc}(n)$ in this case is given by:

$$E_{xc}^{GGA}[n(r)] = \int f[n(r), \nabla n(r)] dr$$  \hspace{1cm} (1.7)

The gradient of the density term results in much better binding energies compared to the LDA so that it makes GGA functionals the most important class of functionals in current DFT.

In summary, the system with electron-electron interactions can be mapped to non-interacting electron system by Kohn-Sham theory, so that the calculation of ground state can be achieved based on the non-interacting model. For an infinite solid bulk, further simplification can be done by periodic assumption. The k-point grid is a computational approach used to approximate integrals of the electron density over the entire unit cell with periodic boundary conditions. The integration is performed in reciprocal space (i.e. in the Brillouin zone) for convenience and efficiency, and the k-point grid is where the electron density is sampled for the integration. The higher the number of sampled points, the more accurate are the approximated integrals. Typically, a Monkhorst-Pack k-point grid, which is essentially a uniformly spaced grid, is used in the Brillouin zone [46]. The Monkhorst-Pack grids are specified as $n_1 \times n_2 \times n_3$ grids, and the total number of k-points is $n_1 \cdot n_2 \cdot n_3$. However, the computational cost is linear in the total number of k-points, so the balance between convergence and computational efficiency needs to be considered.

Based on DFT, we can use the nudged elastic band (NEB) method to locate saddle points and calculate the reaction pathway [47]; this method is a "chain of states" method, where several intermediate states, or images, of the system are connected by springs to map out a reaction pathway between the initial and final states. By selecting an appropriate spring constant, we optimize the intermediate images by including only the parallel component of the spring force and the perpendicular component of the true force. We use several intermediate images for each NEB calculation and optimize these images to yield a minimum energy path. Because these paths are directed by force projection, the energy is not consistent with the force being...
optimized. Therefore, we choose the force-based quick-min optimizer to ensure that the NEB algorithm converges.

The work described in this thesis uses these computational methods to investigate two potential routes to propene: 1. Olefin metathesis of ethene and butene to produce propene, and 2. Catalytic dehydrogenation of CH$_4$ and hydrogenation of CO$_2$ to methanol, and subsequent methanol to olefins (MTO) process as shown in Figure 1.2. Because the MTO process has been well studied, this work focuses on three catalytic conversion: 1) Metathesis of ethene and 2-butene; 2) Methane dehydrogenation; 3) CO$_2$ hydrogenation. We aim to model and explore the catalytic conversion of these carbon-containing compounds to provide fundamental insights on chemical reactions and catalyst design for high activity and selectivity.
Figure 1.2: Two potential routes for propene production
Chapter 2

Formation of Active Sites on Metal Oxide Catalysts

2.1 Introduction

In recent years, the metathesis of ethene (H₂C=CH₂) and 2-butene (H₃C−CH=CH−CH₃) to produce propene (H₂C=CH−CH₃) has attracted widespread interest due to increasing industrial demand for propene, which is an important chemical intermediate used as the building block for commodity chemicals ranging from plastic products to gasoline components as stated in the introduction. The heterogeneous catalysts containing Re, Mo, or W [10, 11, 12, 13, 14] are favored over metathesis catalysis because of the high reactivity of their unpaired d electrons, so that they can adopt multiple oxidation states to form active complexes and lower the activation energy of the metathesis reaction [48]. Handzlik investigated the metathesis activity of Mo methylidene species in zeolites, and revealed that an MoO(CH₂) (metal-carbene) fragment is a vital intermediate, with a high positive change, such that the oxygen site plays an important role in dictating the high catalytic activity [49]. Meanwhile, Luo et al. studied methyltrioxorhenium-catalyzed olefin cyclopropanation, and found that the reaction is catalyzed by the metal Re site by forming a ReO structure [50].

As a metallic compound with W, tungsten trioxide WO₃ has received considerable attention for metathesis reactions, since it can maintain its stable structure within industrial reaction temperature ranges and can be easily deposited using physical or chemical approaches [12, 16, 17, 18]. Several studies are highlighted here. Davazoglou et al. [20] claimed to obtain as equal metathesis activity with well dispersed low loading WO₃/SiO₂ catalysts as with catalysts
of higher tungsten content indicating the importance of obtaining a well dispersed catalyst. Huang et al. [21, 22] prepared a series of WO$_3$ catalysts by the thermal spread method and found that a proportional correlation between tetrahedral tungsten oxide species and metathesis activities. Liu et al. [25] showed that the formation of a surface (hydr)oxide layer on WO$_3$ is accelerated in the presence of a moist atmosphere, and discovered this shortens the calcination time required to produce highly active catalysts. Recently, Chaemchuen et al obtained Raman, UV-Vis and H$_2$-TPR spectra suggesting that WO$_3$ catalysts calcined at 550 °C exhibit high activity for the metathesis of ethene and 2-butene to produce propene [26], so the prospects for industrial-scale propene production via metathesis are extremely promising.

Hérisson and Chauvin were the first to postulate that metathesis can proceed rapidly at modest temperatures through a two step process: 1. Initiation to form metal-carbene active sites [51, 52, 53], and 2. Propagation, including the [2+2] cycloadition of alkene double bonds, at these metal-carbene active sites to form metallocyclobutane intermediates. A number of theoretical investigations [54, 55, 56, 57, 58] and experimental studies [59, 60, 61, 62] have already confirmed the propagation steps in the Hérisson-Chauvin mechanism. However, the process of forming the initial metal-carbene active sites is still not known, due to limitations in detecting the presence and molecular structure of the active sites with current spectroscopic techniques [63]. Thus, we focus here on the formation of these transition metal-alkylidene species that serve as active sites for further propagation steps.

In this work, we employ first-principles calculations based on density functional theory to explore the energetics and kinetics of W-carbene active site formation on WO$_3$ surfaces. Theoretical/computational methods have been previously employed to study metal-catalyzed olefin reactions [64, 65, 66, 67, 68]; they provide fundamental insights that are relatively difficult to obtain experimentally (e.g., determination of the active sites, identification of possible reaction intermediates, nature of the transition states). We use a semi-infinite slab to model the catalyst structure and quantify its activity for olefin metathesis. The use of periodic models avoids the introduction of edge effects and allows for a more accurate description of surface relaxation. The stability of various surface terminations of WO$_3$ are calculated, and the correlation between the coordination of the tungsten and oxygen atoms in the oxide and the strength of gas molecule adsorption is determined. We thus show how the
structure of the catalyst directly influences its activity for olefin metathesis. We also show the preferred pathway to form W-carbene active sites with calculated activation barriers.

2.2 Model and Method

Tungsten trioxide (WO₃) exhibits perovskite-like structures with corner-sharing WO₆ octahedra. However, structural analyses of WO₃ have revealed considerable deviations from the ideal cubic perovskite type, with the majority of these distortions corresponding to antiferroelectric displacements of W atoms and mutual rotations of oxygen octahedra [69]. As in most perovskite-like substances, the magnitude of the distortion depends on the temperature of the sample [70]. WO₃ crystals melt at 1473 °C and undergo five phase transitions over the temperature range from 900 to-180 °C: tetragonal → orthorhombic → monoclinic → triclinic → monoclinic. At 550 °C, bulk WO₃ takes on the orthorhombic phase, and it is at this temperature that WO₃ catalysts have been shown to exhibit high activity for ethene and 2-butene metathesis [71, 72, 26]. While first-principles calculations are typically performed at 0 K, they have been used to model various phases of WO₃, including the orthorhombic phase [73, 74, 75].

We thus use the orthorhombic phase for the WO₃ bulk. Its space group is Pmnb, with 
\[ a = 7.341 \text{ Å}, \ b = 7.570 \text{ Å}, \ c = 7.754 \text{ Å} \] [72]. The deviation from the ideal perovskite structure is characterized by a zigzag motion of the W atomic positions in the \( b \) and \( c \) directions, as well as a tilt system with tilt angles around \( a \) [76].

To build the surface slab models, the WO₃ bulk is cleaved along the (001) surface, which is chosen for consistency [75] with the majority of the published experimental studies on WO₃. The crystal is easily cleaved along the (001) surface since it is layered along this direction as a result of the antiferroelectric distortion of the W sublattice [77, 78]. Thus, good quality single crystals of WO₃ (001) can be prepared by moderate heating in an oxygen-rich atmosphere [79, 80, 81] and characterized using scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and photoelectron spectroscopy (UPS, XPS) [82, 83].

Therefore, the WO₃ (001) surfaces were taken into account in the present study. The WO₃ (001) surface is modeled by a five-layer slab, with the bottom two atomic layers frozen
in the bulk configuration and the top three atomic layers allowed to relax. A \( p \times 2 \times 2 \) supercell is used to ensure that all adsorbates do not interact with their periodic images (i.e., separation by at least 10 Å). The \( \text{WO}_3 \) (001) surface thus consists of four chemically distinguishable types of surface atoms: 1. Fivefold coordinated tungsten \( W_{5c} \), 2. Sixfold coordinated tungsten \( W_{6c} \), 3. Twofold bridging oxygen \( O_{2c} \), and 4. Singly coordinated oxygen \( O_{1c} \) (Figure 2.1).

All calculations are performed within the framework of density functional theory (DFT), using the Vienna Ab Initio Simulation Package (VASP 5.2) [84, 85, 86] and the generalized gradient approximation of Perdew, Burke, and Ernzerhof [87] to represent the exchange-correlation energy. The wavefunctions of the atomic cores are described using the Projector-Augmented Wave method (PAW) method [88, 89], which includes all plane waves with kinetic energies smaller than the chosen cutoff energy of 400 eV. This ensured an energy convergence within \( 1 \times 10^{-5} \) eV, using the conjugate gradient method. We sample the Brillouin zone using a \( 6 \times 6 \times 6 \) Monkhorst-Pack \( \mathbf{k} \)-point mesh for the \( \text{WO}_3 \) bulk [73], and a \( 6 \times 6 \times 1 \) \( \mathbf{k} \)-point mesh for the \( \text{WO}_3 \) surface slab. We observed that spin-polarized calculations did not yield
significant changes to the calculated energies compared to non-spin-polarized calculations [90].

The energy of adsorption, $E_{ads}$, for the olefin molecules on the surface is defined as:

$$E_{ads} = E_{adsorbate+surface} - E_{surface} - E_{adsorbate}$$

where $E_{surface}$ is the total energy of the surface slab, $E_{adsorbate}$ is the total energy of the gas-phase adsorbate, and $E_{adsorbate+surface}$ is the total energy of the composite system. Since the calculations are performed at 0 K and fixed cell volume, the differences in Gibbs free energy should equal the differences in total energy. By this definition, a negative value of $E_{ads}$ corresponds to an exothermic and spontaneous adsorption process. We also assume that the entropic contribution to the Gibbs free energy is negligible since the translational, vibrational, and rotational entropies of the gas-phase adsorbate should not change significantly upon adsorption. Thus, the change in Gibbs free energy with temperature for this system is likely to be small, since $\left(\frac{\partial G}{\partial T}\right)_P = -S$.

To locate saddle points and calculate the reaction pathway, we used the nudged elastic band (NEB) method; By selecting an appropriate spring constant, we optimize the intermediate images by including only the parallel component of the spring force and the perpendicular component of the true force. We use four intermediate images for each NEB calculation and optimize these images to yield a minimum energy path. Because these paths are directed by force projection, the energy is not consistent with the force being optimized. Therefore, we choose the force-based quick-min optimizer to ensure that the NEB algorithm converges. Since we established that calculations at 0 K do not significantly change the Gibbs free energy, we anticipate that the calculated activation energy barriers and reaction pathway should be representative of the true reaction under industrial operating conditions.
2.3 Results

2.3.1 Proposed mechanism for formation of W-carbene active sites

As suggested by the Herisson-Chauvin mechanism, the initiating and propagating intermediates in olefin metathesis are metal-carbene species. These may be formed from either ethene or 2-butene in our reaction. The metathesis reaction proceeds with these two reactants, as shown in Scheme 2.2.

Figure 2.2: The metathesis reaction pathways of ethene and 2-butene to produce propene. (a) Ethene reactant, (b) 2-butene reactant.

2.3.2 Adsorption of ethene and 2-butene on WO$_3$ (001)

Ethene molecules can adsorb on the WO$_3$ (001) surface by single site adsorption (on the O site or W site) or two site adsorption (on the two O sites, two W sites, or one O and one W site). The possible adsorption configurations, after geometry optimization, are shown in Figures 2.3 and 2.4. The calculated energies of adsorption are listed in Table 2.1.

As shown in Table 2.1 for ethene adsorption, the two site adsorption configuration corresponding to W$_{5c}$--C=C--O$_{1c}$ is the most energetically favorable, with $E_{ads} = -26.73$ kJ/mol. By contrast, the configuration corresponding to O$_{1c}$--C=C--O$_{1c}$ is the least energetically favorable, with $E_{ads} = -8.01$ kJ/mol; the low energy of adsorption may be attributed to
Figure 2.3: Optimized geometries, including bond lengths (Å), for ethene adsorbed to WO$_3$ (001).
Figure 2.4: Optimized geometries, including bond lengths (Å), for 2-butene adsorbed to WO$_3$ (001).
Table 2.1: Calculated energies of adsorption for ethene and 2-butene on WO$_3$ (001).

<table>
<thead>
<tr>
<th>Adsorption configuration</th>
<th>ethene $E_{ads}$ (kJ/mol)</th>
<th>2-butene $E_{ads}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Monodentate</td>
<td>Bidentate</td>
</tr>
<tr>
<td>$O_{1c}$···C=C</td>
<td>-22.39</td>
<td>-20.35</td>
</tr>
<tr>
<td>$O_{2c}$···C=C</td>
<td>-3.23</td>
<td>-</td>
</tr>
<tr>
<td>$W_{5c}$···C=C</td>
<td>-21.40</td>
<td>-18.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_{1c}$···C=C···$O_{1c}$</td>
<td>-8.01</td>
<td>-1.74</td>
</tr>
<tr>
<td>$W_{5c}$···C=C···$O_{1c}$</td>
<td>-26.73</td>
<td>-14.18</td>
</tr>
<tr>
<td>$W_{6c}$···C=C···$O_{1c}$</td>
<td>-15.15</td>
<td>-18.24</td>
</tr>
<tr>
<td>$W_{5c}$···C=C···$W_{5c}$</td>
<td>-24.31</td>
<td>-14.38</td>
</tr>
<tr>
<td>$W_{6c}$···C=C···$W_{5c}$</td>
<td>-23.83</td>
<td>-</td>
</tr>
</tbody>
</table>

the large distance separating both $O_{1c}$ sites ($r_{O_{1c}···O_{1c}} = 5.455$ Å), so that ethene cannot physically bond to both oxygen sites. Similarly, the single site adsorption configuration corresponding to $O_{2c}$···C=C is also energetically unfavorable, due to steric repulsion with the adjacent W-oxo site. Thus, we conclude that $W_{5c}$···C=C···$O_{1c}$ ($R_E$) is the most likely configuration for adsorbed ethene on WO$_3$ (001).

For 2-butene, the one site adsorption configuration corresponding to $O_{1c}$···C=C is the most energetically favorable, with $E_{ads} = -20.35$ kJ/mol. Due to steric repulsion from the large methyl groups in 2-butene, two site absorption is not favored; again, the configuration corresponding to $O_{1c}$···C=C···$O_{1c}$ is the least energetically favorable. Thus, we conclude that $O_{1c}$···C=C ($R_B$) is the most likely configuration for adsorbed 2-butene on WO$_3$ (001).

### 2.3.3 Formation of active sites for olefin metathesis

We take the most energetically stable adsorbate configurations – $W_{5c}$···C=C···$O_{1c}$ for ethene and $O_{1c}$···C=C for butene – as our initial state (R) for the metathesis reaction. Since the reaction pathway to form W-carbene active sites involves several intermediates, different potential oxametallacycle intermediates (IM) [91, 92] were postulated by comparison of their adsorption energies, so that together they yield a five-step process (Scheme 2.5).
Figure 2.5: The formation pathway of active sites from ethene and 2-butene on WO₃ (001), respectively (Left: ethene pathway; Right: 2-butene pathway)
Active sites for ethene metathesis

As shown in Figure 2.6, the first intermediate formed by ethene is a six-membered oxametallacycle (IM$_{E1}$) from the initial W$_{5c}$····C=C···O$_{1c}$ reactant, R$_E$. The transition state, TS$_{E1}$, involves olefin activation via migration of hydrogen from ethene to surface-bound O$_{2c}$, so that a weak W$_{6c}$-C bond is formed. The W=O bond increases in length from 1.711 Å in R$_E$ to 1.922 Å in In$_{E1}$. The C$_1$-C$_2$ bond increases in length from 1.330 Å in R$_E$ to 1.455 Å in In$_{E1}$. Two new bonds – W$_{5c}$-C and O$_{1c}$-C – are formed with bond lengths of 2.70 Å and 1.982 Å, respectively. The second intermediate formed by ethene is a three membered W$_{6c}$-C-O ring (IM$_{E2}$). The transition state, TS$_{E2}$, involves the cleavage of the W$_{5c}$-C bond and the formation of a weak W$_{6c}$-C bond. The third intermediate formed by ethene is a four-membered oxametallacycle (IM$_{E3}$). It was obtained by breaking the previous week W$_{6c}$-C bond and forming a new W$_{6c}$-C bond of 2.336 Å with the second C atom. This structure can greatly reduce ring strain. We thus see that the first three transition states – TS$_{E1}$, TS$_{E2}$, and TS$_{E3}$ – consist of nearly flat oxametallacycles, with dihedral angles of 163.5°, 159.7°, and 173.1°, respectively.

The fourth intermediate step involves the formation of the fourth transition state, TS$_{E4}$, which is the decomposition of the four-membered oxametallacycle and the lengthening of the C-C bond. Formaldehyde (H$_2$C=O, methanal) is evolved into the gas phase. Finally, the W$_{6c}$=CH group quickly undergoes hydrogen redistribution via the fifth transition state TS$_{E5}$, to form the final W=CH$_2$ active site, P$_E$, with a W=C bond length of 1.924 Å. The whole process is depicted in Figure 2.6.

Active sites for 2-butene metathesis

The first intermediate formed by 2-butene is a five-membered oxametallacycle (IM$_{B1}$) from the initial O$_{1c}$····C=C reactant, R$_B$. The transition state, TS$_{B1}$, involves olefin activation via migration of hydrogen from 2-butene to surface-bound W$_{5c}$, so that a O$_{2c}$-C bond is formed with bond length 2.032 Å. A O$_{1c}$-C bond is also formed with bond length 2.058 Å. Furthermore, the bond order of W$_{6c}$=O$_{1c}$ is reduced from a double bond to that of a single bond. The second intermediate formed by 2-butene is a four-membered oxametallacycle (IM$_{B2}$). The transition state, TS$_{B2}$, involves the cleavage of the O$_{2c}$-C bond and the formation of
Figure 2.6: Optimized geometries of reactant, intermediates and product for proposed reaction pathway to form $W=CH_2$ active sites via ethene activation. The bond length is in Å.
a W$_{6c}$-C bond to achieve the decomposition of the oxametallacycle. This process may be treated as a [2+2] cycloaddition reaction between the W$_{6c}$-O$_{1c}$ and C$_1$-C$_2$ bonds to form IM$_{B2}$ as the 2-butene moiety moves closer to W$_{6c}$. The third intermediate formed by 2-butene is also a four-membered oxametallacycle (IM$_{B3}$), but involves migration of hydrogen from W$_{5c}$ to O$_{2c}$. Now, we see that IM$_{B3}$ resembles IM$_{E3}$, but that the W$_{6c}$-C bond length is 0.351 Å longer in IM$_{B3}$ than in IM$_{E3}$. The fourth intermediate step involves the formation of the fourth transition state, TS$_{B4}$, which is the decomposition of the four-membered oxametallacycle and the total cleavage of both the original 2-butene C=C bond and the W$_{6c}$-O$_{1c}$. Acetaldehyde (H$_3$C-CH=O, ethanal) is evolved into the gas phase. Finally, the W$_{6c}$=C-CH$_3$ group quickly undergoes hydrogen redistribution via the fifth transition state, TS$_{B5}$, to form the final W=CH–CH$_3$ active site, P$_{B}$, with a W=C bond length of 1.910 Å. The whole process is depicted in Figure 2.7

2.3.4 Activation energies for active site formation

The energy diagram depicting ethene reacting on WO$_3$ (001) to form W=CH$_2$ active sites is presented in Figure 2.8. We normalize the total energy of the constituent components (e.g., gas-phase ethene and clean WO$_3$ (001)) to zero. From Table 2.1, we thus mark the energy of the reactant, R$_E$, to be -26.73 kJ/mol. We see that the formation of the first intermediate, IM$_{E1}$, from the reactant, R$_E$, has a computed activation energy barrier of $E_a = +21.6$ kJ/mol and is endothermic, with $E_{ads} = +6.71$ kJ/mol. The formation of the second intermediate, IM$_{E2}$, has $E_a = +13.48$ kJ/mol and is also endothermic, with $E_{ads} = +8.57$ kJ/mol. The formation of the third intermediate, IM$_{E3}$, has $E_a = +17.03$ kJ/mol and is the first exothermic step, with $E_{ads} = -5.41$ kJ/mol. We note that IM$_{E3}$ consists of the W$_{6c}$···C=C···O$_{1c}$ adsorption configuration first described in Table 2.1, yet IM$_{E3}$ is 1.71 kJ/mol lower in energy than ethylene adsorbed to WO$_3$ (001) in the W$_{6c}$···C=C···O$_{1c}$ configuration. The ”hydrogen effect” stabilizes the hydrocarbon radical via hydrogen co-adsorption, and this effect has also been observed previously for related reactions on oxide surfaces [93, 94, 95, 96, 97, 98, 99]. In the next step, the oxametallacycle ring is opened to form the fourth intermediate, IM$_{E4}$. The final hydrogen redistribution from O$_{2c}$ to the neighboring W=CH site is barrierless, yet the overall process of forming the W-carbene active site is endothermic ($\Delta E = +15.74$ kJ/mol). When comparing all energy barriers in ethene
Figure 2.7: Optimized geometries of reactant, intermediates and product for proposed reaction pathway to form W=CH–CH₃ active sites via 2-butene activation. The bond length is in Å.
pathway, it is easily seen that the oxametallacycle ring opening has the highest activation energy barrier of $E_a = +46.13 \text{ kJ/mol}$.

The energy diagram depicting 2-butene reacting on WO$_3$ (001) to form W=CH–CH$_3$ active sites is also presented in Figure 2.8. Again, we normalize the total energy of the constituent components (e.g., gas-phase 2-butene and clean WO$_3$ (001)) to zero. From Table 2.1, we thus mark the energy of the reactant, $R_B$, to be -17.71 kJ/mol. The formation of the first intermediate, $IM_{B1}$, from the reactant, $R_B$, has the highest activation energy barrier of $E_a = +35.19 \text{ kJ/mol}$ and is endothermic, where $E_{ads} = +14.89 \text{ kJ/mol}$. The second and third intermediates form exothermically, with low activation energy barriers of $E_a = +10.66 \text{ kJ/mol}$ for $TS_{B2}$ and $E_{ads} = +4.28 \text{ kJ/mol}$ for $TS_{B3}$. The decomposition of the four-membered oxametallacycle via $TS_{B4}$ has a relatively high $E_a = +19.23 \text{ kJ/mol}$ and is again endothermic. The final hydrogen redistribution from O$_{2c}$ to the neighboring W=C-CH$_3$ site is barrierless, yet the overall process of forming the W-carbene active site is again endothermic ($\Delta E = +13.14 \text{ kJ/mol}$).

Figure 2.8: Minimum energy paths for ethene (blue) and 2-butene (red), with corresponding activation energies, for W-carbene active site formation on WO$_3$ (001).
2.4 Discussion

We have thus computed pathways for active site formation via ethene and 2-butene activation. Since both sets of metal-carbene species are formed on $W_{6c}$. We know that $IM_{E3}$ and $IM_{B3}$ are more energetically stable than their $IM_{E4}$ and $IM_{B4}$ counterparts in both pathways. Energy must thus be added to these intermediate configurations to cross the activation barriers. Even when hydrogen migrates to unsaturated carbons to form $P_E$ and $P_B$, these final states are also higher in energy than $IM_{E3}$ and $IM_{B3}$, respectively. Thus, these active sites will proceed to react with new ethene or 2-butene molecules easily and quickly in the propagation step of the metathesis process.

Also, we can see that the rate-limiting step in the ethene pathway is the cycloreversion of the four-membered oxametallacycle to release formaldehyde, with the transition state depicted in Figure 2.9. This four-membered ring is particularly energetically stable with little steric repulsion, so the activated hydrocarbons are strongly bound to the oxide surface. Thus, the activation energy barrier is very high (+46.13 kJ/mol). By contrast, the analogous step in the 2-butene pathway, where acetaldehyde is released, has a much lower activation energy barrier (+19.23 kJ/mol). In this pathway, the four-membered ring contains dangling methyl groups that result in unfavorable steric effects with the hydrogenated oxide surface. Thus, the ring-opening reaction is much more energetically favorable in the 2-butene pathway than in the ethene pathway.

Instead, the rate-limiting step in the 2-butene pathway is the electrophilic addition to form the oxametallacycle, with the transition state depicted in Figure 2.9. Although the methyl groups in 2-butene are electron-donating, thus favoring this reaction, the steric effects oppose the electrophilic effects. Thus, the activation energy barrier is very high (+35.19 kJ/mol). By contrast, the steric effects are not present in the ethene pathway, so the activation energy barrier is much lower (+21.6 kJ/mol).

In summary, the 2-butene pathway is projected to be kinetically faster than the ethene pathway to form W-carbene active sites for olefin metathesis, due to the latter’s extremely high activation energy barrier to breaking the oxametallacycle intermediate. This result
Figure 2.9: Transition states for rate limiting steps in ethene (left, blue) and 2-butene (right, red) pathways.
suggests that using a higher ratio of 2-butene to ethene will promote the formation of W-carbene active sites on WO$_3$ catalysts, and enhance the activity of this catalysis for olefin metathesis and propene formation.

2.5 Conclusions

A comprehensive density functional theory study of the mechanisms for forming W-carbene active sites is presented here, in order to lend insight into the metathesis reaction between ethene and 2-butene to form propene on WO$_3$ catalysts. We first show that on the most thermodynamically stable WO$_3$ (001) surface, four chemically distinguishable types of surface atoms are present: fivefold coordinate W$_{5c}$, sixfold coordinate W$_{6c}$, twofold bridging oxygen O$_{2c}$, and singly coordinated oxygen O$_{1c}$. Ethene adsorbs preferentially to the oxide surface in a two-site W$_{5c}$···C−−C···O$_{1c}$ configuration, while 2-butene adsorbs preferentially in a one-site O$_{1c}$···C=C configuration. The reaction pathways for W-carbene active site formation differ between ethene and 2-butene, though both proceed via five-step processes. In the ethene pathway, six-membered, five-membered, and four-membered oxametallacycles are formed successively. However, in the 2-butene pathway, only five-membered and four-membered oxametallacycles are formed. We also find that the opening of the four-membered oxametallacycle is the rate-limiting step of the ethene pathway, while the forming of the five-membered oxametallacycle is the rate-limiting step of the 2-butene pathway. We ultimately find that 2-butene preferentially forms W-carbene active sites, compared to ethene, due to the presence of electrophilic and steric effects that destabilize the intermediates. These results provide us with design guidelines for propene synthesis on WO$_3$ catalysts.
Chapter 3

Propagation of Olefin Metathesis at Active Sites

3.1 Introduction

We have investigated the initiation of olefin metathesis on tungsten trioxide (WO$_3$) catalysts, by showing that trans-2-butene more readily forms W-carbene active sites on the surface, compared to ethene. We now present our analysis of the propagation steps at these active sites.

The propagation includes the [2+2] cycloaddition of (parallel-aligned) alkene double bonds to form metallocyclobutane intermediates at these metal-carbene active sites [51, 52, 53, 100]. Szeto et al. investigated these two processes at low pressure and temperature using WH$_3$ active sites. Two parallel catalytic cycles have been proposed where the cycle involving the less sterically hindered tungstacyclobutane intermediates is most likely favored. It has been found that the arrangement of substituents on the least thermodynamically favored tungstacyclobutane governs the conversion rate of the cross metathesis reaction for propylene production from butenes and/or ethylene [101]. However, the two-step metathesis process has not still been fully understood, and the structure/activity relationships are not clear, due to limitations in experimentally detecting the molecular structure of metal-carbene active sites and metallocyclobutanes with current spectroscopic techniques [59, 60, 61, 62]. First-principles calculations based on density functional theory can complement experimental mechanistic studies, and provide valuable information on the structure of the active centers and the energy of adsorbates interacting with the surfaces [54, 55, 56, 57, 58, 102]. In addition,
detailed reaction pathways can be derived and characterized by the kinetic parameters of the constituent elementary steps [103].

We performed a comprehensive density functional theory study of metathesis initiation on the WO$_3$ (001) surface [104]. We chose the (001) surface because it represented the most thermodynamically stable surface, with a surface energy of formation that is an order of magnitude more stable than the (100), (111), and (110) surfaces, respectively; the WO$_3$ (001) surface has also been formed and characterized experimentally using STM and LEED [82, 81]. Furthermore, the activity of the WO$_3$ catalyst appears to depend strongly on the calcination temperature during catalyst preparation, with catalysts calcined at 550 °C, which exhibit the orthorhombic phase, appearing to be most active. Finally, while the experimental catalysts are typically supported by alumina or silica, these supports are relatively inert, while WO$_3$ is potentially redox active [105, 106]; thus, we chose to first ascertain the catalytic activity of WO$_3$ on olefin metathesis, and left the effect of the support (e.g., via anchoring of individual tungsten-carbene active sites on alumina or silica slabs) as the subject of future work.

We showed that tungsten-carbene active sites readily form on this surface, so that metathesis between ethene and trans-2-butene [26] should be feasible. We revealed that the reaction pathways for W-carbene active site formation differs between ethene and trans-2-butene, though both proceed via five-step processes. In the ethene pathway, six-membered, five-membered, and four-membered (oxa)metallacycles are formed successively. However, in the trans-2-butene pathway, only five-membered and four-membered (oxa)metallacycles are formed. We also found that the opening of the four-membered (oxa)metallacycle is the rate-limiting step of the ethene pathway, while the forming of the five-membered (oxa)metallacycle is the rate-limiting step of the trans-2-butene pathway. We ultimately found that trans-2-butene preferentially forms W-carbene active sites, compared to ethene, due to the presence of electrophilic and steric effects that destabilize the intermediates.

In this work, we studied metathesis propagation on the WO$_3$ (001) surface, as cleaved from the orthorhombic bulk; this allowed for consistency with our previous study [104]. We calculated detailed geometries and energetics of reaction intermediates and products. We modeled various configurations for adsorbed ethene and adsorbed trans-2-butene, and compared the thermodynamic stability of the resulting (oxa)metallacycle species. We studied the pathways of propagation proceeding on the stable W-carbene species and determined the rate-limiting
step. We also developed a thorough kinetic model of the metathesis reaction over the WO$_3$ (001) surface, based on transition-state theory. Such a technique, which explicitly takes into account the entropic contributions, allows us to calculate rate constants for elementary steps and quantify their responses to changes in temperature. These results will hopefully guide the development of more active catalysts and more suitable reaction conditions for propene production.

3.2 Model and Method

3.2.1 Structural optimization

To build the surface slab models, the WO$_3$ bulk is cleaved along the (001) surface, which is also chosen for consistency with our previous study on active sites formation over WO$_3$ [104]. We used a five-layer semi-infinite slab to model the WO$_3$ (001) catalyst structure with W=CH$_2$CH$_3$ active sites. The use of the periodic models avoids the introduction of edge effects and allows for a more accurate description of surface relaxation.

Again, all calculations were performed within the framework of DFT, using VASP 5.2 and the generalized gradient approximation of PBE to represent the exchange-correlation energy. The PAW method, with a 400 eV energy cutoff, was used to describe the wavefunctions of the atomic cores. The tetrahedron method with Blöchl corrections [107] was used to set the partial occupancies for the orbitals. While a $k$-point mesh size of $6 \times 6 \times 1$ was used for the WO$_3$ surface slab in our previous study [104], we ultimately used the $3 \times 3 \times 1$ Γ-centered Monkhorst-Pack $k$-point mesh for the WO$_3$ surface with W=CH$_2$CH$_3$ active sites, which still gave results that were sufficiently converged (within $1 \times 10^{-5}$ eV using the conjugate gradient method). We observed that spin-polarized calculations did not yield significant changes to the calculated energies compared to non-spin-polarized calculations [90].

We optimized the structure of active sites W=CH$_2$CH$_3$ to get a W=C bond length of 1.918 Å, and a C−C bond length of 1.496 Å. A $p\,(2 \times 2)$ supercell was used to ensure that all adsorbates do not interact with their periodic images (i.e., separation by at least 10 Å). The WO$_3$
Figure 3.1: Geometry-optimized WO$_3$ (001) surface with W=CHCH$_3$ active site. Because of the repeated W$_{6c}$–O$_{2c}$–W$_{5c}$ structural motif on the surface, we employ a side view to represent the supercell.

(001) surface with W=CH$_2$CH$_3$ active sites thus consists of five chemically distinguishable types of surface atoms (Figure 3.1):

1. Fivefold coordinated tungsten W$_{5c}$
2. Sixfold coordinated tungsten W$_{6c}$
3. Twofold bridging oxygen O$_{2c}$
4. Active site carbon C$_{A1}$ binding to surface W$_{6c}$ atom
5. Active site carbon C$_{A2}$ from CH$_3$ group

### 3.2.2 Energetics of activation and reaction

The energy of adsorption, $E_{ads}$, for the olefin molecules on the surface is defined as:

$$E_{ads} = E_{adsorbate + surface} - E_{surface} - E_{adsorbate}$$
where $E_{\text{surface}}$ is the total energy of the surface slab, $E_{\text{adsorbate}}$ is the total energy of the gas-phase adsorbate, and $E_{\text{adsorbate+surface}}$ is the total energy of the composite system. Since the calculations are performed at 0 K and fixed cell volume, the differences in Gibbs free energy should equal the differences in total energy. By this definition, a negative value of $E_{\text{ads}}$ corresponds to an exothermic and spontaneous adsorption process.

For calculating energies of adsorption, the inclusion of an empirical dispersion correction [108] appeared to affect the total energies of all reactant and product species almost equally; for example, the energy of adsorption for ethene changed only from -20.75 kJ/mol to -23.86 kJ/mol upon addition of the dispersion correction, and no change in the preferred site for adsorption was noted. Thus, for comparing trends in energies of adsorption in this catalytic system, the uncorrected PBE functional should be sufficient, and again, would provide consistency with our previous study on metathesis initiation [104].

We also assume that for surface-mediated reactions, the change in Gibbs free energy with temperature can be quantified as $\left(\frac{\partial G}{\partial T}\right)_P = S$, which we can assume is primarily due to the vibrational component. We thus carried out a vibrational analysis in order to validate the optimized geometry of the adsorbed species and transition states. All W atoms were rigidly constrained during these calculations. The Hessian dynamical matrix was obtained by numerical differentiation of the forces and diagonalized, which provided the harmonic molecular frequencies and the normal modes. These calculations made it possible to compute zero-point energy (ZPE) corrected energies and vibrational partition functions.

### 3.2.3 Kinetics of reaction

DFT calculation is based on 0 K. However, we can use vibrational frequency results from DFT to predict the rate constant of elementary step at finite temperature by partition function expression. According to the statistics mechanism, the pre-exponential factor, $A$, can be calculated from the entropy differences between the initial and transition states of the respective elementary step, as shown below in Equation 3.1:

$$A(T) = \left(\frac{k_B T}{\hbar}\right) \left(\frac{Q_{TS}}{Q_0}\right)$$  \hspace{1cm} (3.1)
where \( Q_{TS} \) and \( Q_0 \) are the partition functions of transition states and initial states, respectively. \( k_B \) is Boltzmann’s constant, and \( \hbar \) is Planck’s constant. The partition functions themselves are approximated with the vibrational contribution being dominant.

The mathematical and thermodynamical calculations above then enable us to obtain the relationship between reaction rate constants and temperature by the Arrhenius form in Equation 3.2, using the calculated \( E_{a,f}(T) \) and \( A(T) \):

\[
k(T) = A(T) \exp \left( -\frac{E_{a,f}}{k_B T} \right)
\]

Similarly, we can calculate the reverse rate constant by substituting instead \( E_{a,r}(T) \).

### 3.3 Results and Discussion

#### 3.3.1 Proposed mechanism for propagation of olefin metathesis to propene on W-carbene active sites

During metathesis propagation, \( W=\text{CHCH}_3 \) first reacts with ethene to form propene and \( W=\text{CH}_2 \), which then further reacts with *trans*-2-butene to yield the second propene molecule. Our previous study on W-carbene active site formation showed that *trans*-2-butene preferentially reacts with sixfold coordinated tungsten at the surface to form a \( W=\text{CHCH}_3 \) active site [104]; *trans*-2-butene is favored over ethene due to the presence of electrophilic and steric effects that destabilize the intermediates. Therefore, the \( W=\text{CHCH}_3 \) active site is the initial state of the propagation cycle, as shown in Figure 3.2.

Thus, we propose that the first stage of propagation is composed of ethene [2+2] cycloaddition at the \( W=\text{CHCH}_3 \) active site and cycloreversion of the first (oxa)metallacycle to form the first propene molecule, and the second stage is composed of *trans*-2-butene [2+2] cycloaddition at the \( W=\text{CH}_2 \) active site and cycloreversion of the second (oxa)metallacycle to form the second propene molecule. The (oxa)metallacycle may be either the four-membered ring with \( W_{6c} \) and carbon, five-membered ring with \( W_{6c}, O_{1c} \) and carbon, or six-membered ring with \( W_{6c}, W_{5c} \) and carbon. In the following section, we present optimized (oxa)metallacycle
Figure 3.2: The proposed mechanism of metathesis propagation on WO$_3$(001) catalysts, starting from W=CHCH$_3$ active site. Reactants, intermediates and products are shown.
structures for each stage of propagation, model propagation on WO₃ (001) catalysts and determine the rate-limiting step, and investigate the thermal kinetics at each stage of the propagation cycle by calculating the rate constants of elementary steps.

3.3.2 Propagation of ethene for metathesis

Ethene adsorption on W=CHCH₃ active site

As propagation is defined as the redistribution of fragments of alkenes by the scission and regeneration of carbon-carbon double bonds, the ethene molecule should bind to the W=CHCH₃ active site by [2+2] cycloaddition of two carbon-carbon double bonds. In our calculations, the free ethene is in gas phase, so we study ethene adsorption to the surface prior to the reaction. The adsorption of ethene molecules, with their Cₑ₁ and Cₑ₂ atoms, at the W=CHCH₃ active site can proceed by three types of two-site adsorption:

(A) Cᴬ₁···Cₑ₂=Cₑ₁···W₆c: Cₑ₁ and Cₑ₂ adsorb to sixfold coordinated tungsten W₆c and active site carbon Cᴬ₁, respectively

(B) Cᴬ₁···Cₑ₂=Cₑ₁···O₂c: Cₑ₁ and Cₑ₂ adsorb to twofold coordinated oxygen O₂c and active site carbon Cᴬ₁, respectively

(C) Cᴬ₁···Cₑ₂=Cₑ₁···W₅c: Cₑ₁ adsorbs to fivefold coordinated tungsten W₅c, while Cₑ₂ adsorbs to Cᴬ₁

S₁ denotes Stage 1 of the propagation process, and IN denotes the initial state for propagation.

After geometry optimization, the ethene molecule moves in space to find the most energetically stable adsorption structures and energies. The corresponding configurations are shown in Figure 3.3. For Cᴬ₁···Cₑ₂=Cₑ₁···W₆c adsorption, corresponding to (A)-type binding, the ethene molecule in vertical orientation tilts slightly relative to the orientation of W₆c−Cᴬ₁. It leads to a four-membered ring, S₁IN−W₆c, which includes four active atoms, W₆c, Cᴬ₁, Cₑ₁, and Cₑ₂. For (B)-type binding, it produces a five-membered ring, S₁IN−O₂c,
Figure 3.3: Adsorption configurations and energies for ethene on WO$_3$ (001) with W=CHCH$_3$ active site. C$_{E1}$ and C$_{E2}$ denote two carbon atoms in ethene. C$_{A1}$ and C$_{A2}$ denotes two carbon atoms in active site. S$_1$ denotes Stage 1 of the propagation process, and IN denotes the initial state for propagation.

which includes five active atoms, W$_{6c}$, C$_{A1}$, C$_{E1}$, C$_{E2}$, and surface O$_{2c}$. For (C)-type binding C$_{A1}$···C$_{E2}$=C$_{E1}$···W$_{5c}$, the six-membered (oxa)metallacycle ring S$_1$IN=W$_{5c}$ is formed.

Figure 3.3 and Table 3.1 show that the (C)-type binding configuration is the most energetically favorable, with corresponding bond lengths shown in Table 3.2. Both the W$_{6c}$−C$_{A1}$ and C$_{E1}$−C$_{E2}$ bonds in the (C)-type binding configuration are elongated compared to their values prior to adsorption; this suggests that the molecule is activated. The (A)-type binding configuration is slightly less energetically favorable, even though the W=C bond at the surface and the C=C bond in the ethene molecule are even longer than that in the other adsorption configurations. This may be attributed to the small four membered ring inducing a stronger steric effect than the six membered ring, such that the overlapping electron clouds result in elongation of the W=C bond in the (A)-type binding configuration to reduce the cost in energy. By comparing the area formed by the rings, using all obtained data on bond lengths, we can conclude that the location where there is less shielding reduces the net intermolecular forces acting on the ethene molecule; thus, the (C)-type binding configuration is relatively stable compared to the (A)-type binding configuration. By contrast, the (B)-type binding configuration to form a five-membered ring is the least energetically favorable. The ethene molecule is only slightly activated, and the low energy of adsorption may be attributed to the weak interaction between oxygen atoms in metal oxide and carbons
atom in the alkene. This suggests that tungsten atoms are more active than oxygen atoms for small alkene propagation on the WO₃ (001) surface. For all configurations, the methyl group has not been affected upon adsorption and only moves slightly away (≈ 0.01 – 0.02 Å) from the carbon atom of the metal-carbene active site.

To ensure that we have a complete understanding of ethene behavior in the surface, we have also considered single site adsorption of the molecule. All of the calculated adsorption energies are also shown in Table 3.1. We found the single site absorption configurations are generally energetically unfavorable compared to the corresponding two site adsorption configurations. As it does not appear that this pathway would be preferred for propagation, we will not discuss it further here, although they could be explored as the subject of future work on side reactions to the main Hérisson-Chauvin mechanism.

Table 3.1: Calculated energies of adsorption for ethene and 2-butene cycloaddition on WO₃ (001) with W-carbene active sites.

<table>
<thead>
<tr>
<th>Adsorption configuration</th>
<th>ethene $E_{ads}$ (kJ/mol)</th>
<th>2-butene $E_{ads}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two site binding</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{active\ site} \cdots C=\cdots W_{6c}$</td>
<td>-19.59</td>
<td>-0.29</td>
</tr>
<tr>
<td>$C_{active\ site} \cdots C=\cdots O_{2c}$</td>
<td>-17.33</td>
<td>-8.91</td>
</tr>
<tr>
<td>$C_{active\ site} \cdots C=\cdots W_{5c}$</td>
<td>-20.75</td>
<td>-12.35</td>
</tr>
<tr>
<td>One site binding</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$W_{6c} \cdots C=\cdots C$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>$W_{5c} \cdots C=\cdots C$</td>
<td>-17.31</td>
<td>-9.82</td>
</tr>
<tr>
<td>$O_{2c} \cdots C=\cdots C$</td>
<td>-4.26</td>
<td>-2.07</td>
</tr>
<tr>
<td>$C_{active\ site} \cdots C=\cdots C$</td>
<td>-7.23</td>
<td>-3.46</td>
</tr>
</tbody>
</table>

**Formation and cycloreversion of the C₄ (oxa)metallacycle**

Adsorbed ethene reacts with a W=CHCH₃ active site to form a C₄ (four carbon atoms in total) (oxa)metallacycle species by [2+2] cycloaddition. Based on three type of adsorption configurations, three possible C₄ (oxa)metallacycles can be obtained, as shown in Figure 3.4:

- (oxa)metallacycle species $S_{1}IM-W_{6c}$ from ethene [2+2] cycloaddition on adsorption sites $C_{A1}$ and $W_{6c}$
Figure 3.4: Optimized structures of oxametallacycles from ethene [2+2] cycloaddition on WO$_3$ (001) with W=CHCH$_3$ active site. $S_1$ denotes Stage 1 of the propagation process, and IM denotes the intermediate.

- (oxa)metallacycle species $S_1$IM$^-$$O_{2c}$ from ethene cycloaddition on adsorption sites $C_{A1}$ and $O_{2c}$
- (oxa)metallacycle species $S_1$IM$^-$$W_{5c}$ from ethene cycloaddition on adsorption sites $C_{A1}$ and $W_{5c}$

The $S_1$ represents Stage 1 as mentioned above, TS denotes transition state, and IM denotes intermediate.

Table 3.2: Calculated changes in bond lengths upon ethene adsorption at W-carbene active sites, and formation and cycloreversion of (oxa)metallacycles

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>$W=C$ (Å)</th>
<th>$C_{E1} - C_{E2}$ (Å)</th>
<th>$W-C_{E1}$ or $O-C_{E1}$ (Å)</th>
<th>$C_{A1} - C_{E2}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before adsorption</td>
<td>1.918</td>
<td>1.339</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A): $S_1$IN$^-$$W_{6c}$</td>
<td>2.033</td>
<td>1.381</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B): $S_1$IN$^-$$O_{2c}$</td>
<td>2.018</td>
<td>1.352</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C): $S_1$IN$^-$$W_{5c}$</td>
<td>1.992</td>
<td>1.367</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_1$IN$^-$$W_{6c}$</td>
<td>2.154</td>
<td>1.492</td>
<td>2.013</td>
<td>1.896</td>
</tr>
<tr>
<td>$S_1$IN$^-$$O_{2c}$</td>
<td>2.113</td>
<td>1.375</td>
<td>1.868</td>
<td>1.973</td>
</tr>
<tr>
<td>$S_1$IN$^-$$W_{5c}$</td>
<td>2.089</td>
<td>1.489</td>
<td>2.245</td>
<td>1.822</td>
</tr>
<tr>
<td>Cycloreversion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_1$IN$^-$$W_{6c}$</td>
<td>1.924</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_1$IN$^-$$O_{2c}$</td>
<td>1.924</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$S_1$IN$^-$$W_{5c}$</td>
<td>1.924</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2 again gives the bond lengths upon formation of the C₄ (oxa)metallacycle. Most of the (oxa)metallacycle pathways significantly activate the C=C bond of ethene, except for the S₁IM−O₂c (oxa)metallacycle species. We note that for the S₁IM−W₅c (oxa)metallacycle species, the Cₐ₁−Cₑ₂−Cₑ₁ bond is nearly linear, with a C−C−C angle of 163.1°.

In order to proceed to propagation, the intermediate C₄ (oxa)metallacycle species must be decomposed by cycloreversion to yield a propene molecule; thus, only a methylene compound remains on the surface. Because we have three different (oxa)metallacycle intermediates, S₁IM−W₆c, S₁IM−O₂c, and S₁IM−W₅c, there exist three possible paths to the product in Stage 1. We used the CI-NEB method, with transition states between the three initial adsorption configurations and three C₄ (oxa)metallacycle intermediates, and between the C₄ (oxa)metallacycle intermediates and W=CH₂ + propene, to map out stationary points along the minimum energy paths. Three transition states, S₁TS₁−W₆c, S₁TS₁−O₂c and S₁TS₁−W₅c, in the cycloaddition step, and three transition states, S₁TS₂−W₆c, S₁TS₂−O₂c and S₁TS₂−W₅c, in the cycloreversion step, were identified as corresponding to the closing and opening of a four, five or six-membered (oxa)metallacycle ring.

Table 3.3: Calculated energies of activation and energies of reaction for (oxa)metallacycle formation and cycloreversion steps during ethene propagation

<table>
<thead>
<tr>
<th>Adsorption configuration</th>
<th>Formation</th>
<th>Cycloreversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ea (kJ/mol)</td>
<td>ΔErxn (kJ/mol)</td>
</tr>
<tr>
<td>(A): S₁IN−W₆c</td>
<td>+43.6</td>
<td>+23.8</td>
</tr>
<tr>
<td>(B): S₁IN−O₂c</td>
<td>+91.2</td>
<td>+49.8</td>
</tr>
<tr>
<td>(C): S₁IN−W₅c</td>
<td>+61.6</td>
<td>+37.6</td>
</tr>
</tbody>
</table>

The energy diagram depicting the ethene propagation stage on WO₃ (001) with W=CHCH₃ active sites is presented in Figure 3.5, with specific energies of adsorption and energies of reaction in Table 3.3. We normalized the total energy of ethene, 2-butene and clean WO₃ (001) with W=CHCH₃ active sites to zero. We denoted adsorption configurations (S₁IN−W₆c, S₁IN−O₂c and S₁IN−W₅c) as W=CHCH₃−ethene(ad). For the Cₐ₁ and O₂c binding pathway, the formation of the five-membered (oxa)metallacycle species S₁IM−O₂c has the highest activation barrier and the most endothermic reaction energy. However, for
the C\textsubscript{A1} and W\textsubscript{5c} binding pathway, the decomposition of the six-membered (oxa)metallacycle species S\textsubscript{1}IM−W\textsubscript{5c}, has the highest activation energy barrier. When comparing all energy barriers in ethene propagation, it is easily seen that the C\textsubscript{A1} and W\textsubscript{6c} binding pathway, with the four-membered (oxa)metallacycle intermediate, has the lowest activation energy barriers in both the [2+2] cycloaddition step and the cycloreversion step. It indicates the small (oxa)metallacycle ring is more active, with stronger electron interaction. This favorable activation energy barrier for C\textsubscript{A1} and W\textsubscript{6c} interaction should be sufficient to overcome a small penalty (1.14 kJ/mol) for the overall energy of formation compared to the C\textsubscript{A1} and W\textsubscript{5c} interaction. Therefore, ethene preferentially forms a four-membered C\textsubscript{4} (oxa)metallacycle intermediate by [2+2] cycloaddition at C\textsubscript{A1} and W\textsubscript{6c}, then proceeds to cycloreversion to produce another W=CH\textsubscript{2} active site for further propagation.

The detailed structures of the reaction species involved in the C\textsubscript{A1} and W\textsubscript{6c} (A)-type pathway, including transition states, are shown in Figure 3.6, with bond lengths listed in Table 3.2. We can see the length of the W\textsubscript{6c}−C\textsubscript{A1} and C\textsubscript{E1}−C\textsubscript{E2} bonds increase along the propagation pathway, while the distances between C\textsubscript{A1} and C\textsubscript{E2}, and between W\textsubscript{6c} and C\textsubscript{E1}, decrease. For the transition state S\textsubscript{1}TS\textsubscript{1}−W\textsubscript{6c}, the C\textsubscript{A1}−C\textsubscript{A2} bond is still almost in vertical orientation,

Figure 3.5: Minimum energy paths for ethene propagation at Stage 1 by binding to C\textsubscript{A1} and W\textsubscript{6c} (black), C\textsubscript{A1} and O\textsubscript{2c} (red), and C\textsubscript{A1} and W\textsubscript{5c} (blue); and for 2-butene propagation at Stage 2 by binding to C\textsubscript{E1} and W\textsubscript{5c} (blue), and C\textsubscript{E1} and O\textsubscript{2c} (red).

The detailed structures of the reaction species involved in the C\textsubscript{A1} and W\textsubscript{6c} (A)-type pathway, including transition states, are shown in Figure 3.6, with bond lengths listed in Table 3.2.
Figure 3.6: Optimized structures of the initial state, transition states, intermediate and product along the minimum energy pathway for ethene propagation. The red dashed line denotes the formed bond with decreasing length along the path, and the blue dashed line denotes the broken bond with increasing length along the path.

although it tilts slightly relative to the surface normal, while the $W_{6c} - C_{E1}$ bond is formed with a length of 2.150 Å. The resulting four-membered ring has a $W - C - C - C$ dihedral angle of 142.7°. For the transition state $S_1TS_2 - W_{6c}$, the $W - C - C - C$ dihedral angle changes to 165.8°, and the bond length of $W_{6c} - C_{E1}$ decreases to 1.968 Å; both are characteristic of the re-formation of the $W=C$ bond. The dihedral angle of the intermediate $S_1IM - W_{6c}$ is 149.6°. Thus the structure of $S_1IM - W_{6c}$ is likened to a puckered ring, rather than a flat four membered (oxa)metallacycle ring. The methylene compound $W=CH_2$ ($S_1P$) is obtained by the breaking of $W_{6c} - C_{A1}$ and $C_{E1} - C_{E2}$ to release one propene molecule. The $W=CH_2$ now becomes a new $W_{6c}$ active site for propagation in Stage 2.
3.3.3 Propagation of \textit{trans}-2-butene for metathesis

\textit{trans}-2-butene adsorption on \(\text{W}=\text{CH}_2\) active site

2-Butene is an acyclic alkene with four carbon atoms. It exists as two geometrical isomers: \textit{cis}-2-butene and \textit{trans}-2-butene. The \textit{cis}-isomer has the two methyl groups on the same side of the alkene bond, while the \textit{trans}-isomer has the two methyl groups on opposite sides of the alkene bond. The steric crowding between the methyl groups causes the \textit{cis}-isomer to be less stable than the \textit{trans}-isomer. Thus, we use \textit{trans}-2-butene as the olefin reactant for the study on the second stage of the metathesis reaction between ethene and 2-butene, which is also in agreement with industrial practices and recent experimental work. [26, 109, 110]. In the following part of this paper, 2-butene represents \textit{trans}-2-butene for convenience.

Similar to the study on the ethene propagation stage, we first investigate \textit{trans}-2-butene adsorption on the surface with \(\text{W}=\text{CH}_2\) active site. The possible two-site adsorption configurations for \textit{trans}-2-butene are:

\begin{enumerate}
  \item[(A)] \(\text{C}_{\text{E1}}\cdots\text{C}_{\text{B2}}\!=\!=\!\text{C}_{\text{B1}}\cdots\text{W}_6\!\!\!\text{c}\) \(\text{C}_{\text{B1}}\) and \(\text{C}_{\text{B2}}\) adsorb to sixfold coordinated tungsten \(\text{W}_6\!\!\!\text{c}\) and active site carbon \(\text{C}_{\text{E1}}\), respectively. \(\text{C}_{\text{B1}}\) and \(\text{C}_{\text{B2}}\) denote two doubly bonded carbons (i.e., secondary carbon atom and tertiary carbon atom) in \textit{trans}-2-butene.

  \item[(B)] \(\text{C}_{\text{E1}}\cdots\text{C}_{\text{B2}}\!=\!=\!\text{C}_{\text{B1}}\cdots\text{O}_2\!\!\!\text{c}\) \(\text{C}_{\text{B1}}\) and \(\text{C}_{\text{B2}}\) adsorb to twofold coordinated oxygen \(\text{O}_2\!\!\!\text{c}\) and active site carbon atom \(\text{C}_{\text{E1}}\), respectively.

  \item[(C)] \(\text{C}_{\text{E1}}\cdots\text{C}_{\text{B2}}\!=\!=\!\text{C}_{\text{B1}}\cdots\text{W}_5\!\!\!\text{c}\) \(\text{C}_{\text{B1}}\) adsorbs to fivefold coordinated tungsten \(\text{W}_5\!\!\!\text{c}\) while \(\text{C}_{\text{B2}}\) adsorbs to \(\text{C}_{\text{E1}}\).
\end{enumerate}

\(\text{S}_2\) denotes Stage 2 of the propagation process.

The optimized structures corresponding to these configurations are shown in Figure 3.7. For \(\text{C}_{\text{E1}}\cdots\text{C}_{\text{B2}}\!=\!=\!\text{C}_{\text{B1}}\cdots\text{W}_6\!\!\!\text{c}\) adsorption, corresponding to (A)-type binding, a four membered ring \(\text{S}_2\!\!\!\text{IN}\!\!\!\text{W}_6\!\!\!\text{c}\) is formed, which includes four active atoms, \(\text{W}_6\!\!\!\text{c}, \text{C}_{\text{E1}}, \text{C}_{\text{B1}},\) and \(\text{C}_{\text{B2}}\). For \(\text{C}_{\text{E1}}\cdots\text{C}_{\text{B2}}\!=\!=\!\text{C}_{\text{B1}}\cdots\text{O}_2\!\!\!\text{c}\) adsorption, corresponding to (B)-type binding, a five-membered ring \(\text{S}_2\!\!\!\text{IN}\!\!\!\text{O}_2\!\!\!\text{c}\) is produced, which includes five active atoms \(\text{W}_6\!\!\!\text{c}, \text{C}_{\text{E1}}, \text{C}_{\text{B1}}, \text{C}_{\text{B2}},\) and surface \(\text{O}_2\!\!\!\text{c}\).
Figure 3.7: Adsorption configurations and energies for 2-butene on WO$_3$ (001) with W=CH$_2$ active site. C$_{B1}$ and C$_{B2}$ denote two doubly bonded carbons in 2-butene (secondary carbon atom and tertiary carbon atom in 2-butene). C$_{B1*}$ and C$_{B2*}$ represent carbon atoms in the non-binding methyl groups. S$_2$ denotes Stage 2 of the propagation process, and IN denotes the initial state for propagation.

For C$_{E1}$…C$_{B2}$=C$_{B1}$…W$_{5c}$ adsorption, corresponding to (C)-type binding, the six-membered (oxa)metallacycle ring S$_2$IN–W$_{5c}$ is formed.

As shown in Figure 3.7 and Table 3.1, the strongest adsorption configuration corresponds to the (C)-type binding configuration, with the (B)-type binding configuration being slightly less favored and the (A)-type binding configuration resulting in essentially zero adsorption. This last result can be explained by steric hindrance between the methyl groups in trans-2-butene and the W=CH$_2$ group. The inactive methyl groups require enough physical space given their electrostatics; thus, they hinder the process of trans-2-butene adsorption to the catalyst surface.

Table 3.4 shows that in the (C)-type binding configuration, the W=C bond at the surface and C=C bond in the trans-2-butene molecule are only slightly elongated relative to their values prior to adsorption. Thus, we confirm that trans-2-butene adsorption on W=CH$_2$ is weaker than ethene adsorption on W=CHCH$_3$. The steric effect produced by inactive methyl groups in trans-2-butene not only destabilizes the adsorbate, but even hinders bond activation in trans-2-butene. Thus, initiating the trans-2-butene stage of propagation may be the rate-limiting step of the reaction pathway.
Table 3.4: Calculated changes in bond lengths upon trans-2-butene adsorption at W-carbene active sites, and formation and cycloreversion of (oxa)metallacycles

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>W=C (Å)</th>
<th>C_{B1}−C_{B2} (Å)</th>
<th>W−C_{B1} or O−C_{B1} (Å)</th>
<th>C_{E1}−C_{B2} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before adsorption</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A): S_2IN−W_{6c}</td>
<td>1.933</td>
<td>1.329</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B): S_2IN−O_{2c}</td>
<td>1.927</td>
<td>1.335</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C): S_2IN−W_{5c}</td>
<td>1.929</td>
<td>1.338</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S_2IN−O_{2c}</td>
<td>2.005</td>
<td>1.435</td>
<td>1.899</td>
<td>1.532</td>
</tr>
<tr>
<td>S_2IN−W_{5c}</td>
<td>1.998</td>
<td>1.517</td>
<td>2.225</td>
<td>1.575</td>
</tr>
<tr>
<td>Cycloreversion</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S_2IN−O_{2c}</td>
<td>1.935</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S_2IN−W_{5c}</td>
<td>1.935</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For the strongest adsorption configuration, S_2IN−W_{5c}, the W_{6c}−C_{E1} bond is 1.929 Å, which is almost the same as the bond length of 1.924 Å observed in clean W=CH$_2$ active site. The C_{B1}−C_{B2} bond is only slightly elongated to 1.338 Å from 1.329 Å, which is the bond length of ethene in the gas phase. Compared with the energies and the change of bond lengths for ethene adsorption in Stage 1, we can see that 2-butene adsorption on W=CH$_2$ is weaker than ethene adsorption on W=CHCH$_3$. The steric effect produced by inactive methyl groups in 2-butene not only destabilizes the adsorbate, but even stabilizes 2-butene against bond activation.

The experimental findings of Chaemchuen et al. [26] suggested that trans-2-butene was the dominant reactant during this olefin metathesis process, and other researchers [109, 110] have also supported this finding. However, we note that cis-2-butene may also have been detected experimentally as a side product of this reaction. For completeness, we modeled the adsorption of cis-2-butene on the W-carbene active site, and found that the energy of adsorption was a little less ($E_{ads} = -12.35$ kJ/mol) than that for trans-2-butene adsorption. We believe that this difference is due to the steric crowding between the methyl groups, which causes the cis stereoisomer to be less stable than the trans-stereoisomer. While we stick to the Hérisson-Chauvin mechanism here, we note that the inclusion of cis-2-butene in a full microkinetic model could be the subject of future work.
Formation and cycloreversion of the C₅ oxametallacycle

Adsorbed trans-2-butene reacts with W-CH₂ active site to form a C₅ (five carbon atoms in total) (oxa)metallacycle species by [2+2] cycloaddition. Because of the weak adsorption of S₂IN-W₆c, and difficulty in optimizing the structure of the C₅ (oxa)metallacycle due to steric hindrance, we no longer consider trans-2-butene cycloaddition on that site. Based on two remaining types of adsorption configurations, two possible C₅ (oxa)metallacycles can be obtained, as shown in Figure 3.8:

- (oxa)metallacycle species S₂IM−O₂c from trans-2-butene cycloaddition on adsorption sites Cₑ₁ and O₂c
- (oxa)metallacycle species S₂IM−W₅c from trans-2-butene cycloaddition on adsorption sites Cₑ₁ and W₅c

The S₂ represents Stage 2 as mentioned above, TS denotes a transition state, and IM denotes an intermediate.

Table 3.4 again gives the bond lengths upon formation of the C₅ (oxa)metallacycle. Compared to the elongation of bonds in ethene [2+2] cycloaddition, we can conclude there is less electron transfer from trans-2-butene to W-carbene than from ethene to W-carbene, and hence, the catalytic activation is lower for this step of the propagation process.

Table 3.5: Calculated energies of activation and energies of reaction for (oxa)metallacycle formation and cycloreversion steps during trans-2-butene propagation

<table>
<thead>
<tr>
<th>Adsorption configuration</th>
<th>Formation</th>
<th>Cycloreversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eₐ (kJ/mol)</td>
<td>ΔE_rxn (kJ/mol)</td>
</tr>
<tr>
<td>(B): S₂IN−O₂c</td>
<td>+108.3</td>
<td>+32.7</td>
</tr>
<tr>
<td>(C): S₂IN−W₅c</td>
<td>+88.7</td>
<td>+11.6</td>
</tr>
</tbody>
</table>

For oxametallacycle species S₂IM−O₂c, the W₆c−Cₐ₁ bond is slightly elongated to 2.005 Å, compared to 1.927 Å in adsorption configuration S₂IN−O₂c. The C₉₁−C₉₂ bond also is
Figure 3.8: Optimized structures of oxametallacycles from 2-butene [2+2] cycloaddition on WO$_3$ (001) with W–CH$_2$ active site. $S_2$ denotes Stage 2 of the propagation process, and IM denotes the intermediate.

The newly formed bonds, $C_{E1}–C_{B2}$ and $O_{2c}–C_{B1}$, are 1.532 Å and 1.899 Å, respectively. For oxametallacycle species $S_2IM–W_{5c}$, the $C_{E1}–C_{E2}$ bond increases to 1.517 Å, which is 0.18 Å longer than the bond in $S_2IN–W_{5c}$. However, the $W_{6c}–C_{E1}$ bond length of 1.998 Å is almost the same as that in the adsorption state. The newly formed bonds, $C_{E1}–C_{B2}$ and $W_{5c}–C_{B1}$, are 1.575 Å and 2.225 Å, respectively, in length. Compared with the elongation of bonds in ethene [2+2] cycloaddition, we can conclude there is less electron transfer from 2-butene to W-carbene than from ethene to W-carbene.

To complete the propagation cycle, the intermediate $C_5$ (oxa)metallacycle species then is decomposed by cycloreversion to yield the second propene molecule and regenerate the initial W=CHCH$_3$ active site. Because we have two (oxa)metallacycle intermediates, $S_2IM–O_{2c}$ and $S_2IM–W_{5c}$, there exist two possible paths for $trans$-2-butene propagation. Again, we used the CI-NEB method to map out stationary points along these two pathways. Two transition states, $S_2TS_1–O_{2c}$ and $S_2TS_1–W_{5c}$, in the [2+2] cycloaddition step, and two transition states, $S_2TS_2–O_{2c}$ and $S_2TS_2–W_{5c}$, in the cycloreversion step, are identified as corresponding to the closing and opening of the five and six-membered (oxa)metallacycle rings.
The energy diagram depicting the trans-2-butene propagation state on WO$_3$ (001) with W=CH$_2$ active sites is presented in Figure 3.5, with specific energies of adsorption and energies of reaction in Table 3.5. When comparing all energy barriers in trans-2-butene propagation, we find that the C$_E$ and W$_{5c}$ binding pathway, with its six-membered (oxa)metallacycle intermediate, has the lower activation energy barriers in both the [2+2] cycloaddition step and the cycloreversion step. Therefore, in Stage 2, trans-2-butene preferentially forms a six-membered C$_E$ (oxa)metallacycle intermediate by [2+2] cycloaddition at C$_E$ and W$_{5c}$, and then proceeds to cycloreversion to regenerate the initial active site W=CHCH$_3$ and complete the propagation cycle. The overall heat of reaction associated with trans-2-butene propagation in this stage is estimated to be $\Delta H_{\text{rxn}} = -28.91$ kJ/mol. If we compare the preferred energy pathway in Stage 2 with the pathway in Stage 1, we find the highest energy barrier corresponds to the formation of the six-membered (oxa)metallacycle species, S$_2$IM−W$_{5c}$, for trans-2-butene propagation, with the activation energy of $E_a = +88.71$ kJ/mol; this is 17.39 kJ/mol larger than the corresponding energy barrier for the decomposition of the S$_1$IM−W$_{6c}$ intermediate in cycloreversion step for ethene propagation. Therefore, the formation of the six-membered (oxa)metallacycle species S$_2$IM−W$_{5c}$ in Stage 2 appears to be the rate determining step for the whole propagation cycle.

The detailed structure of the reaction species involved in the C$_E$ and W$_{5c}$ (C)-type pathway, including transition states, are shown in Figure 3.9, with bond lengths listed in Table 3.4. Due to the overlap of several atoms in the side view of the S$_2$TS$_1$−W$_{5c}$ transition state, we have not explicitly labeled the bond lengths; however, we observe similar changes in bond lengths in Stages 1 and 2. Compared to the twisted structure of S$_2$TS$_1$−W$_{5c}$, the S$_2$TS$_2$−W$_{5c}$ transition state consists of a nearly flat (oxa)metallacycle, with a dihedral angle of 166.8$^\circ$. We can see that the initial reactant, trans-2-butene, for Stage 2 of the propagation cycle, isomerizes to the cis-2-butene structure during the [2+2] cycloaddition step. This structural conversion can greatly reduce surface strain on the inactive methyl groups and stabilize the six-membered C$_E$ (oxa)metallacycle intermediate. However, it also leads to artificially higher energies of activation for the "elementary step", as shown in Figure 3.5. The second propene product is obtained by breaking the previously elongated W$_{6c}$−C$_E$ and C$_B$−C$_B$ bonds. This completes the propagation cycle by regenerating the W=CHCH$_3$ active site for Stage 1 of propagation. We notice, however, that the W=CHCH$_3$ active site regeneration, while structurally similar due to periodic boundary conditions, is not at the same surface W atom. In fact, the cycloreversion produces the W=CHCH$_3$ species at an originally-labeled
W\textsubscript{5c} site, instead of at an originally-labeled W\textsubscript{6c} site site. This fivefold coordinated W\textsubscript{5c} thus becomes a new sixfold coordinated tungsten W\textsubscript{6c} site, due to the formation of W\textsubscript{5c}−C\textsubscript{B2}. We show this difference using "*" in S\textsubscript{1}P (Figure 3.9). This active site migration may explain the low deactivation of the WO\textsubscript{3} catalyst and its high activity for metathesis of ethene and trans-2-butene.

### 3.3.4 Rate constants for propagation cycle

On the basis of the aforementioned potential energy profiles, depicted in Figure 3.5, for propagation of ethene and trans-2-butene on the tungsten trioxide (WO\textsubscript{3}) (001) surface, we demonstrated that the activation energy barrier for [2+2] cycloaddition of trans-2-butene to form the six-membered C\textsubscript{5} (oxa)metallacycle ring is much higher than other elementary steps. For this reason, we hypothesize that this is the rate limiting step of propagation, and proceeded to calculate the forward and reverse rate constants for this process. We used the frequencies of the (oxa)metallacycle intermediates and their corresponding transition states.
to calculate our best predictions for temperature-dependent rate constants of each forward and reverse step in the two stages of propagation.

As the temperature is increased from 300 K to 1000 K, as shown in Figure 3.12, the rate constant of the forward reaction (i.e., [2+2] cycloaddition of trans-2-butene) increases from \( k_f(300 \text{ K}) = 1.39 \times 10^{-9} \text{ s}^{-1} \) to \( k_f(1000 \text{ K}) = 2.93 \times 10^{-8} \text{ s}^{-1} \), while the rate constant of the reverse reaction increases from \( k_r(300 \text{ K}) = 3.89 \times 10^{-9} \text{ s}^{-1} \) to \( k_r(1000 \text{ K}) = 1.71 \times 10^{-8} \text{ s}^{-1} \).

When the temperature is below about 750 K, the decomposition rate of the six-membered ring (\( S_2 \text{IM} - W_{5c} \)) is faster than the [2+2] cycloaddition of trans-2-butene. However, the cycloaddition rate constant is more sensitive to temperature, due to its larger activation energy. The cycloaddition thus becomes faster than the decomposition when the temperature is higher than 750 K.

The \( k \) vs. \( T \) relation for stage 1 and the second step of stage 2 also have been plotted as shown in Figures 3.10, 3.11, and 3.13. For [2+2] cycloaddition of ethene, the forward reaction rate constant increases almost linearly from \( k_f(300 \text{ K}) = 1.57 \times 10^{-6} \text{ s}^{-1} \) to \( k_f(1000 \text{ K}) = 3.73 \times 10^{-5} \text{ s}^{-1} \), while the reverse reaction rate constant increases from \( k_r(300 \text{ K}) = 7.09 \times 10^{-6} \text{ s}^{-1} \) to \( k_r(1000 \text{ K}) = 2.58 \times 10^{-5} \text{ s}^{-1} \). For [2+2] cycloreversion of the \( C_4 \) (oxa)metallacycle, the forward reaction rate constant increases from \( k_f(300 \text{ K}) = 2.12 \times 10^{-8} \text{ s}^{-1} \) to \( k_f(1000 \text{ K}) = 6.43 \times 10^{-7} \text{ s}^{-1} \), while the reverse reaction rate constant slowly increases from \( k_r(300 \text{ K}) = 1.42 \times 10^{-7} \text{ s}^{-1} \) to \( k_r(1000 \text{ K}) = 4.68 \times 10^{-7} \text{ s}^{-1} \). For [2+2] cycloreversion of \( C_5 \) (oxa)metallacycle, the forward reaction rate constant changes from \( k_f(300 \text{ K}) = 9.13 \times 10^{-6} \text{ s}^{-1} \) to \( k_f(1000 \text{ K}) = 5.24 \times 10^{-5} \text{ s}^{-1} \), while the reverse reaction rate constant increases from \( k_r(300 \text{ K}) = 1.33 \times 10^{-6} \text{ s}^{-1} \) to \( k_r(1000 \text{ K}) = 3.94 \times 10^{-6} \text{ s}^{-1} \).

All of these rate constants are at least an order of magnitude larger than the rate constant of the rate limiting step, which we concluded was the [2+2] cycloaddition of trans-2-butene; thus, we find good agreement with the results from the energy barriers calculated at 0 K.

We further analyzed the free energy at 750 K. The free energy diagram depicting the stage 1 ethene propagation on \( \text{WO}_3 \) (001) with \( \text{W}=\text{CHCH}_3 \) active sites, and the stage 2 trans-2-butene propagation on \( \text{WO}_3 \) (001) with \( \text{W}=\text{CH}_2 \) active sites, is presented in Figure 3.14. We normalized the free energy of \( S_2 \text{IM} - O_{5c} \) to zero. Although the free energy of activation of [2+2] cycloaddition of trans-2-butene at stage 2 displays a lower barrier by 9.4 kJ/mol, compared with the data for the total energy profile at 0 K, the barrier height for the [2+2]
Figure 3.10: Reaction rate constants, as a function of temperature, of forward and reverse reactions for ethene propagation: Formation of C₄ (oxa)metallacycle.

Figure 3.11: Reaction rate constants, as a function of temperature, of forward and reverse reactions for ethene propagation: Cycloreversion of C₄ (oxa)metallacycle.
Figure 3.12: Reaction rate constants, as a function of temperature, of forward and reverse reactions for 2-butene propagation: Formation of C₅ (oxa)metallacycle.

Figure 3.13: Reaction rate constants, as a function of temperature, of forward and reverse reactions for 2-butene propagation: Cycloreversion of C₄ (oxa)metallacycle.
cycloaddition of trans-2-butene is still the largest, which demonstrates again that this is the rate-limiting step.

![Graph](image)

**Figure 3.14:** Calculated free energy profile for Stage 1 (black) and Stage 2 (blue) of propagation at 750 K.

We note that the activation energy for [2+2] cycloreversion of the C₅ (oxa)metallacycle is lower than the activation energy for the reverse reaction of [2+2] cycloaddition of trans-2-butene, so the propagation can occur even if the temperature falls below 750 K. However, the 750 K threshold is still significant, because if there is an excess of propene product (that has been produced in stage 1), the last step may become slow even it has a low barrier. In this case, the cycloreversion of S₂IM-O₅c may hinder the reaction if the temperature is below 750 K. Therefore, we suggest 750 K as the lower bound for efficient metathesis of ethene and trans-2-butene, and this temperature is corroborated by the 300-500 °C temperature range explored by Chaemchuen et al., and the optimal 90% conversion and 95% selectivity for propene obtained by reaction at 500 °C [26].

While lateral adsorbate-adsorbate interactions may influence the stability of (oxa)metallacycle intermediates and the kinetics of reaction on the surface with high coverage, we believe that under typical reaction conditions for olefin metathesis, the total surface coverage should be low. Thus, all adsorption energies and activation energies are assumed to be coverage-independent, and reaction rate constants should not be affected much by the surface coverage.
3.3.5 Conclusions

We have performed a comprehensive density functional theory study of the mechanism for propene production over tungsten trioxide (WO$_3$) catalysts, based on propagation of ethene at W=CHCH$_3$ sites and trans-2-butene at W=CH$_2$ sites. In validating the Hérisson-Chauvin mechanism for olefin metathesis, we showed that ethene propagation occurs by [2+2] cycloaddition at the C$_{A1}$ and W$_{6c}$ sites, followed by cycloreversion of the C$_4$(oxa)metallacycle to produce another W=CH$_2$ active site for further propagation. We also showed that trans-2-butene propagation occurs by [2+2] cycloaddition at the C$_{E1}$ and W$_{5c}$ sites, followed by cycloreversion of the C$_5$(oxa)metallacycle to regenerate the W=CHCH$_3$ active site. While it may be argued that ethene adsorption at the W$_{5c}$ site is slightly favored energetically compared to the W$_{6c}$ site, the latter possesses much more favorable activation and kinetic pathway for propene production. Furthermore, we showed that the W=CH$_2$ sites are less active in the propagation process compared to W=CHCH$_3$, such that the rate limiting step is the [2+2] cycloaddition of trans-2-butene to form the six-membered C$_5$ (oxa)metallacycle ring. When the temperature is below 750 K, the decomposition rate of the six-membered ring S$_2$IM$-$W$_{5c}$ is faster than the [2+2] cycloaddition of trans-2-butene. However, the cycloaddition rate constant is more sensitive to temperature due to its larger activation energy. The cycloaddition becomes faster than the decomposition when temperature is over 750 K, which we suggest as the lower bound for the reaction temperature by which successful metathesis of ethene and trans-2-butene to produce propene may be achieved. We assert that these results lay the foundation for future studies on the kinetics of initiation and propagation, including the role of the catalyst support on the electronic structure of the metal-carbene active site and the effect of the cis-2-butene side product on the reaction mechanism, and guide the development of more active and selective catalysts for propene production.
Chapter 4

C–H Bond Activation on Metal Nanoclusters

4.1 Introduction

Methane holds great promise as a valuable building block for the production of chemicals and liquid fuels, primarily because of its relative abundance in both natural gas reserves and agricultural byproducts. However, the development of technologies for efficient and cost-effective methane conversion is still an ongoing process, primarily because of the chemical stability of methane in the gas phase. Several methods for utilizing methane currently exist, including synthesis gas [111, 112, 113, 114] and alcohol production using steam reforming and/or selective oxidation processes. These methods provide compelling environmentally-friendly [115] and potentially energetically-efficient alternatives to the direct combustion of methane as fuel.

However, these processes require the activation, and possibly dissociation, of at least one carbon-hydrogen bond. Many catalysts, including supported transition metal [116, 117, 118] and precious metal [119, 120, 121, 122, 123, 124] nanoparticles, have been shown to efficiently dehydrogenate methane. For instance, dry reforming of methane is well-established even though the overall process is highly endothermic ($\Delta H = +247$ kJ/mol for the following reaction [125]: $nCO_2 + nCH_4 \rightarrow 2nCO + 2nH_2$) due to the thermal stability of carbon dioxide. Synthesis gas production is just one of many methane utilization processes that must operate under high temperatures, and use spherical catalyst particles that are stable under these operating conditions.
However, if we consider also low temperature processes, a world of possibilities is opened up for us to tune the catalyst size and shape to enhance reactivity. In particular, the effect of catalyst size on reactivity has been extensively explored using experimental [126, 127] and theoretical [128, 129, 130] methods. For example, subnanometer-sized platinum clusters, consisting of 8-10 atoms deposited on an alumina support, have been recently shown to increase the turnover frequency (TOF) for the conversion of propane to propylene by 40-100 times more than that of larger catalyst particles [131]. These nanoclusters may assume various shapes depending on the processing conditions, and are still reactive even when placed in conditions other than ultrahigh vacuum [132]. In a related study, the calcination of nanometer-sized platinum particles at different temperatures resulted in two types of particles – at 475 K, tetrahedral particles were preferentially produced, and at 575 K, spherical particles were preferentially produced [127]; the only other shape of platinum synthesized to date is the octahedron. Furthermore, faceted platinum nanoparticles have been shown to keep their shape upon deposition onto alumina supports at temperatures below 350 °C; above this temperature, the particles morph into anisotropic spheroids [133].

By selectively controlling the processing conditions and the shape of the catalyst particles, researchers have achieved increased activity and selectivity in hydrocarbon transformations. The subnanometer platinum clusters described above were shown to selectively activate carbon-hydrogen bonds instead of carbon-carbon bonds at their undercoordinated edge sites [131]. Furthermore, the tetrahedral particles have been shown to promote the isomerization of trans olefins to cis olefins, whereas the spherical particles have been shown to promote the isomerization of cis olefins to trans olefins [127]. These studies suggest that catalyst shapes with an abundance of undercoordinated edge sites, such as tetrahedra and octahedra, may result in enhanced catalytic activity and selectivity.

We thus hypothesize that similar enhancements in catalytic activity and selectivity may occur for methane dehydrogenation on faceted platinum nanoclusters compared to spherical platinum nanoclusters. Other researchers have already explored the effect of cluster size, by comparing the selectivity of methane dehydrogenation on a single platinum atom versus a four-atom platinum nanocluster using theoretical methods [134]. Here, we focus on two platinum clusters roughly 1 nanometer in diameter – a 21-atom hemisphere and a 20-atom tetrahedron (with exposed Pt (111) facets) – and calculate the thermodynamics of all four carbon-hydrogen bond scission steps in methane dehydrogenation to form a methyl group.
(CH\textsubscript{3}), methylene (CH\textsubscript{2}), methyldyne (CH), and carbon atom (C), successively. The hemispherical cluster is chosen to mimic the shape of a spherical cluster upon deposition onto a support, thus creating a flat interface. The magic cluster size of 20 atoms has been demonstrated previously to prefer the tetrahedral or pyramidal shape [135]. For the purposes of this study, only the cluster shape is being varied to isolate the effect of undercoordinated edge and vertex adsorption sites on catalytic reactivity, and the flat interface is kept fixed to mimic its behavior on a support. The support itself is not included for this reason, but its effect on catalytic activity and selectivity will be explored in a future study.

4.2 Model and Method

All molecular species described below were placed within the confines of a cubic box 20 Å in length, in order to ensure at least 10 Å of vacuum between neighboring images in all directions. Geometry optimizations were performed using the conjugate gradient method to minimize the force on each atom, and only the Γ k-point was sampled in reciprocal space.

Two platinum clusters – a 21-atom hemisphere and a 20-atom tetrahedron – were modeled as representative of nanometer-sized catalysts. The Pt\textsubscript{21} hemisphere is composed of three atomic layers, containing 12, 5, and 4 atoms, respectively. The 12-atom layer was kept fixed to maintain the hemispherical shape, while the other two atomic layers were free to move in space. The Pt\textsubscript{20} tetrahedron is composed of four atomic layers, containing 10, 6, 3, and 1 atoms, respectively. All atoms were free to move in space, yet the cluster still retained its metastable tetrahedral shape during all calculations.

Hemispherical Pt\textsubscript{21} contains four types of adsorption sites: 1. Atop (adsorbate binds to only one platinum atom), 2. Bridge (adsorbate binds to two adjacent platinum atoms), 3. FCC/HCP (adsorbate binds at the interstice formed by three close-packed platinum atoms), and 4. Vertex (adsorbates binds at the interstice formed by the four platinum atoms in the topmost atomic layer). All sites are depicted in Figure 4.1.

Tetrahedral Pt\textsubscript{20} contains three types of adsorption sites: 1. Atop (adsorbate binds to only one platinum atom), 2. Bridge (adsorbate binds to two adjacent platinum atoms), and 3. FCC/HCP (adsorbate binds at the interstice formed by three close-packed platinum atoms).
Figure 4.1: Potential CH$_x$ ($x = 0 - 4$) adsorption sites on a hemispherical Pt$_{21}$ nanocluster. Atop sites have the adsorbate binding to only one platinum atom, Bridge sites have the adsorbate binding to two adjacent platinum atoms, FCC/HCP sites have the adsorbate binding at the interstice formed by three close-packed platinum atoms, and Vertex sites have the adsorbate binding at the interstice formed by the four platinum atoms in the topmost atomic layer.

These sites are located at the vertices, edges, and sides of the tetrahedron. For this study, the six considered were: 1. Vertex atop, 2. Edge atop, 3. Edge bridge, 4. Side atop, 5. Side bridge, and 6. Side FCC/HCP. All sites are depicted in Figure 4.2.

Methane (CH$_4$) and its dehydrogenated derivatives – methyl group (CH$_3$), methylene (CH$_2$), methylidyne (CH), and carbon atom (C) – were initially placed 2.5 Å above each of the four adsorption sites on Pt$_{21}$ and each of the six adsorption sites on Pt$_{20}$, and then allowed to move in space to find the most energetically stable adsorption structures and energies. In several cases, the adsorbates migrated from their initial sites to one of the other sites, and these will be described in more detail in the Results and Discussion.

Energies of adsorption were calculated from the total energies of the composite system as well as the isolated Pt$_x$ ($x = 20$ or $21$) and CH$_y$ ($y = 2$, $3$, or $4$):

$$E_{ads} = E_{Pt_x - CH_y} - (E_{Pt_x} + E_{CH_y})$$  \hspace{1cm} (4.1)
Figure 4.2: Potential CH_x (x = 0 – 4) adsorption sites on a tetrahedral Pt_{20} nanocluster. Atop sites have the adsorbate binding to only one platinum atom, Bridge sites have the adsorbate binding to two adjacent platinum atoms, and FCC/HCP sites have the adsorbate binding at the interstice formed by three close-packed platinum atoms. These sites are located at the vertices, edges, and sides of the tetrahedron.

In separate calculations, CH_3, CH_2, CH, and C were also coadsorbed with the equivalent number of hydrogen atoms (one, two, three, and four, respectively) to maintain stoichiometric equivalence with CH_4. The energies of dehydrogenation were calculated from the total energies of the composite system as well as the isolated Pt_x (x = 20 or 21) and CH_4:

$$E_{dehydr} = E_{Pt_x-CH_y-H_{4-y}} - (E_{Pt_x} + E_{CH_4})$$  (4.2)

To locate transition states and calculate the energies of activation and resulting reaction pathways, we used the climbing-image nudged elastic band (CI-NEB) method [47, 136], with four images between the initial and final states, to map out the minimum energy paths for each of the dehydrogenation steps on the two platinum nanoclusters. The CI-NEB method works by driving the highest energy image up to the exact saddle point. This image does not feel the spring force along the band; rather, the true force at this image along the tangent is inverted so that the image maximizes its energy along the band and minimizes its energy in all other directions.
We expected that the scission of the first C-H bond would be the rate-limiting step in methane activation and eventual conversion to liquid fuels. We also expected that each CH$_y$ species would migrate to their energetically favored adsorption sites following dissociation. We generated intermediate images for CH$_{4-y}$+yH adsorbed near the CH$_{3-y}$+($y+1$)H adsorption site, and then generated minimum energy paths connecting the initial image to the intermediate image and the intermediate image to the final image. Each calculation contains four images that are initially generated using linear interpolation, and allowed to relax to the minimum energy path by including only the parallel component of the spring force and the perpendicular component of the true force. Because these paths are directed by force projection, the energy is not necessarily consistent with the force being optimized; thus we choose the force-based quick-min optimizer to ensure the convergence of the nudged elastic band algorithm. The time step employed is 0.01 fs.

4.3 Results and Discussion

4.3.1 CH$_x$ adsorption to Hemispherical Pt$_{21}$

We find that methane (CH$_4$) adsorbs only to an atop site on the Pt$_{21}$ hemisphere, since it migrates off of bridge, FCC/HCP, and vertex sites to adjacent atop sites. The calculated energy of adsorption is $E_{ads} = -0.10$ eV (-9.5 kJ/mol), and this value is consistent with that reported by Viñes et al. [130] for the Pt$_{79}$ hemisphere ($E_{ads} = -7$ kJ/mol). Both our calculated energy of adsorption and Viñes’ energy of adsorption are slightly larger than the corresponding energy of adsorption for methane on a semi-infinite Pt (111) slab (reported as $E_{ads} \approx 0$ kJ/mol [122]). We conclude that the Pt clusters adsorb methane more strongly than Pt slabs due to the undercoordination of the atop sites in the hemispherical clusters, which have only four Pt nearest neighbors compared to six Pt nearest neighbors in Pt (111).

The methyl group (CH$_3$) adsorbs more strongly than methane to Pt$_{21}$, and also prefers the atop site. The calculated energy of adsorption is $E_{ads} = -3.28$ eV (-316 kJ/mol), which is higher than the corresponding energy of adsorption for the methyl group on a semi-infinite Pt (111) slab ($E_{ads} = -168$ kJ/mol [130]). No other adsorption sites are observed, for the methyl group migrates off all bridge, FCC/HCP, and vertex sites to adjacent atop sites. By
adsorbing to an atop site, the methyl group achieves fourfold coordination [128, 137, 138] of its carbon atom by forming a Pt-C bond.

By the same fulfillment of fourfold coordination, methylene (CH$_2$) binds to a bridge site of Pt$_{21}$ to form two Pt-C bonds. The calculated energy of adsorption is $E_{ads} = -5.61$ eV (-542 kJ/mol), which is over 100 kJ/mol stronger than the corresponding energy of adsorption for methylene on a semi-infinite Pt (111) slab [130, 137]. No other adsorption sites are observed, including the atop sites preferred by methylene when adsorbing to Pt (111).

Methylidyne (CH) binds to an FCC/HCP site of Pt$_{21}$ to form three Pt-C bonds. The calculated energy of adsorption is $E_{ads} = -7.30$ eV (-702 kJ/mol). The carbon atom (C) remains at the FCC/HCP, and the calculated energy of adsorption is $E_{ads} = -9.01$ eV (-869 kJ/mol). Energies of adsorption for both methylidyne and the carbon atom atop vertex sites are at least 60 kJ/mol lower than at FCC/HCP sites. All energies of adsorption are summarized in Table 4.1.

Table 4.1: Energies of adsorption (eV) for CH$_x$ ($x = 0 - 4$) on a hemispherical Pt$_{21}$ nanocluster. The asterisk (*) denotes that no adsorption was observed for that particular site.

<table>
<thead>
<tr>
<th></th>
<th>CH$_4$</th>
<th>CH$_3$</th>
<th>CH$_2$</th>
<th>CH</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertex</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>-6.67</td>
<td>-7.99</td>
</tr>
<tr>
<td>Atop</td>
<td>-0.10</td>
<td>-3.27</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Bridge</td>
<td>*</td>
<td>*</td>
<td>-5.62</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>FCC/HCP</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>-7.30</td>
<td>-9.01</td>
</tr>
</tbody>
</table>

The energies of activation and energies of dehydrogenation for the four C-H bond scission steps on Pt$_{21}$, to form CH$_3$ + H, CH$_2$ + 2H, CH + 3H, and C + 4H, are summarized in Figure 4.3; the catalyst systems depicted represent the optimized structures. The calculated energies of activation range from 0.4 eV for the first C-H bond scission, to form CH$_3$ + H, to 1.0 eV for the fourth C-H bond scission to form C + 4H. Furthermore, all bond scissions are energetically downhill except for this fourth C-H bond scission, which suggests that methane dehydrogenation terminates at the formation of CH + 3H.
4.3.2 $\text{CH}_x$ adsorption to Tetrahedral Pt$_{20}$

We find that methane adsorbs preferentially to a vertex atop site on the Pt$_{20}$ tetrahedron, possibly to minimize steric hindrance between the hydrogen atoms of methane and the platinum atoms. The calculated energy of adsorption is $E_{\text{ads}} = -0.17$ eV (-16.7 kJ/mol) is roughly twice that calculated on the Pt$_{21}$ hemisphere. We also observed very weak methane adsorption at the edge bridge site, where $E_{\text{ads}} = -0.02$ eV (-2 kJ/mol). Thus, the edge bridge site on a tetrahedral cluster shows some proclivity towards hydrocarbon adsorption, which has not been previously mentioned in the literature [121, 122, 123, 129, 130, 137].

The methyl group adsorbs most strongly to an edge bridge site, where the calculated energy of adsorption is $E_{\text{ads}} = -3.16$ eV (-306 kJ/mol). The Pt-Pt distance at the edge bridge site increases from 2.52 Å to 2.62 Å upon methyl group adsorption to facilitate the formation of two long Pt-C bonds. We also observed weaker methyl group adsorption on the vertex atop, edge atop, and side atop sites, with all $E_{\text{ads}} \approx -2.8$ eV (-270 kJ/mol).

Methylene readily adsorbs to the edge bridge site, with $E_{\text{ads}} = -5.80$ eV (-559 kJ/mol), but adsorption is also observed on the side bridge site, with $E_{\text{ads}} = -5.31$ eV (-512 kJ/mol). The Pt-Pt distance at the edge bridge site increases from 2.52 Å to 2.59 Å, but the Pt-Pt distance at the side bridge site decreases from 2.65 Å to 2.57 Å.
Methylidyne binds to a side FCC site of Pt$_{20}$ to form three Pt-C bonds. The calculated energy of adsorption is $E_{ads} = -7.45$ eV (-719 kJ/mol). The carbon atom (C) remains at the side FCC site, and the calculated energy of adsorption is $E_{ads} = -8.69$ eV (-838 kJ/mol). We see that the adsorption on the FCC site is slightly more favorable than that on the HCP site, but the differences are only on the order of 20 kJ/mol, which may be within the statistical accuracy of DFT calculations. Strong energies of adsorption are also observed for CH and C on the edge bridge sites (-7.33 eV and -8.41 eV, respectively), but side FCC site offers the highest coordination possible with platinum atoms for these species. All energies of adsorption are summarized in Table 4.2.

Table 4.2: Energies of adsorption (eV) for CH$_x$ ($x = 0$ – 4) on a tetrahedral Pt$_{20}$ nanocluster. The asterisk (*) denotes that no adsorption was observed for that particular site.

<table>
<thead>
<tr>
<th>Site</th>
<th>CH$_4$</th>
<th>CH$_3$</th>
<th>CH$_2$</th>
<th>CH</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertex</td>
<td>-0.17</td>
<td>-2.84</td>
<td>-4.21</td>
<td>-5.19</td>
<td>-6.39</td>
</tr>
<tr>
<td>Edge Atop</td>
<td>*</td>
<td>-2.81</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Edge Bridge</td>
<td>-0.02</td>
<td>-3.16</td>
<td>-5.80</td>
<td>-7.33</td>
<td>-8.41</td>
</tr>
<tr>
<td>Side Atop</td>
<td>-0.02</td>
<td>-2.82</td>
<td>*</td>
<td>*</td>
<td>-6.51</td>
</tr>
<tr>
<td>Side Bridge</td>
<td>*</td>
<td>*</td>
<td>-5.31</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Side FCC</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>-7.45</td>
<td>-8.69</td>
</tr>
<tr>
<td>Side HCP</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>-7.13</td>
<td>-8.45</td>
</tr>
</tbody>
</table>

The energies of activation and energies of dehydrogenation for the four C-H bond scission steps on Pt$_{20}$, to form CH$_3$ + H, CH$_2$ + 2H, CH + 3H, and C + 4H, are summarized in Figure 4.4; the catalyst systems depicted represent the optimized structures. The calculated energies of activation range from 0.2 eV for the second C-H bond scission, to form CH$_2$+2H, to 0.7 eV for the third C-H bond scission to form CH+3H. Again, all bond scissions are energetically downhill except for the fourth C-H bond scission, which suggests that methane dehydrogenation terminates at the formation of CH+3H and may even terminate at the formation of CH$_2$+2H at low temperatures.

We have also compared our energies of activation on the two platinum nanoclusters to published results on various noble metal and transition metal surfaces; these results are summarized in Table 4.3. We see that platinum and palladium catalysts yield the lowest
energy barriers for the dehydrogenation reaction, with the Pt (110) surface exhibiting the most similar set of activation energies to our hemispherical platinum cluster [139].

Table 4.3: Comparison of the energies of activation (eV) for the successive dehydrogenation of methane on metal catalysts. In our work, the tetrahedral cluster has exposed Pt (111) facets. The asterisk (*) denotes that no energy of adsorption was reported.

<table>
<thead>
<tr>
<th>Dehydrogenation step</th>
<th>This work</th>
<th>Pt (110)</th>
<th>Rh (111)</th>
<th>Ni (111)</th>
<th>Ru (0001)</th>
<th>Pd (110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ → CH₃ + H</td>
<td>0.39</td>
<td>0.35</td>
<td>1.04</td>
<td>0.88</td>
<td>0.69</td>
<td>0.79</td>
</tr>
<tr>
<td>CH₃ → CH₂ + 2H</td>
<td>0.45</td>
<td>0.34</td>
<td>0.78</td>
<td>0.51</td>
<td>0.42</td>
<td>0.52</td>
</tr>
<tr>
<td>CH₂ → CH + 3H</td>
<td>0.59</td>
<td>0.56</td>
<td>0.31</td>
<td>0.17</td>
<td>*</td>
<td>0.20</td>
</tr>
<tr>
<td>CH → C + 4H</td>
<td>1.04</td>
<td>1.20</td>
<td>1.40</td>
<td>1.12</td>
<td>*</td>
<td>0.52</td>
</tr>
</tbody>
</table>

4.3.3 Implications for Methane Dehydrogenation

The results from coadsorbing dehydrogenated methane derivatives (e.g., methyl group, methylene, methylidyne, and carbon) and hydrogen atoms on the two platinum nanoclusters suggest that C-H bond scission is more active with faceted metal nanoclusters. The low-coordinated adsorption sites at the vertices and edges of these nanoclusters favor Pt-C bond
formation to donate excess electron density to the adsorbates. Figure 4.5 depicts the calculated charge density for the bare Pt, CH$_3$-Pt, and CH$_2$-Pt catalyst systems, and clearly shows the increased charge density at the edges and vertices of the tetrahedral Pt nanoclusters.

The first C-H bond scission step is widely considered to be the rate-limiting step [130, 140] in methane activation and conversion to liquid fuels. By comparing the energies of activation for this reaction on both nanoclusters, we see that they differ by only 0.03 eV, or approximately $kT$ at room temperature. Thus, there is little effect of the catalyst shape on this first C-H bond scission.

Where the faceted tetrahedral nanocluster shines is the second C-H bond scission, where the energy of activation is 0.25 eV less than the corresponding energy of activation on the hemispherical nanocluster. Using the Arrhenius form of the rate expression, $k = A \exp(-E_a/kT)$, and assuming that the pre-exponential factors $A$ are similar, we can conclude that the reaction proceeds up to 18,000 times faster at room temperature on the tetrahedral cluster than the hemispherical cluster so that more hydrogen is produced. This prediction could be easily verified by measuring the volume fraction of hydrogen gas eluted from a packed bed reactor impregnated with either catalyst system. Thus, shaped catalysts open up the possibility of using lower temperatures for methane dehydrogenation and hydrogen production, provided that the initial C-H bond scission is achieved.

Furthermore, we believe that the tetrahedral nanocluster pushes the dehydrogenation reaction towards the production of methylene and hydrogen. By effectively providing each dissociated species with its own exposed Pt (111) facet, the tetrahedral cluster offers physical separation between the hydrogen atoms and prevents back recombination of the hydrogen and CH$_y$ species.

Lastly, we see that the energy of activation for the third C-H bond scission on the tetrahedral nanocluster is almost double that for the first C-H bond scission. This result is likely due to the energetic stability of the methyl group and the methylene group when adsorbed to the edge bridge site of the tetrahedral cluster, such that further dehydrogenation is not energetically favored. So, we may be able to achieve selective C-H bond breaking to form only the methylene group and hydrogen by controlling the temperature of the reaction. This would not be possible on the hemispherical nanocluster, where the energies of activation for the first three C-H bond scissions are roughly comparable in magnitude. Hence, shaped
Figure 4.5: Charge density for the bare Pt, CH$_3$-Pt, and CH$_2$-Pt catalyst systems. Red indicates increased electronic charge density and Blue indicates decreased electronic charge density.
catalysts also offer the possibility of selective C-H bond scission to form usable building blocks for the synthesis of chemicals and fuels.

We believe that faceted particles may facilitate the production of liquid fuels and higher-chain hydrocarbons using methylene groups as building blocks for insertion into existing hydrocarbon chains. Since faceted particles are stable only at temperatures below 350 °C, additional experimental and theoretical/computational studies are necessary to determine if the kinetics of the carbon-hydrogen bond scission steps are favorable at these temperatures. Nevertheless, shape-selective catalysis opens up new avenues of hydrocarbon transformations that have not been previously observed on noble metal surfaces or spherical nanoparticles.

4.4 Summary

The energies of activation for methane dehydrogenation on platinum nanoclusters have been reduced by controlling the shape of these nanoclusters. Tetrahedral nanoclusters lower the energies of activation for carbon-hydrogen bond scission compared to hemispherical nanoclusters. While the energetics of the first carbon-hydrogen bond scission are comparable on both clusters, the energetics of the second carbon-hydrogen bond scission are much more favorable on the tetrahedral nanocluster, which suggests that the reaction may proceed further to completion even at low temperatures. Furthermore, we may be able use the operating temperature to selectively form methylene groups as building blocks for the synthesis of chemicals and fuels. Thus, we conclude that while spherical noble metal particles may be used to catalyze high temperature processes for producing synthesis gas from methane, faceted noble metal particles may ultimately prove invaluable in facilitating active and selective hydrocarbon transformations at low temperatures.
Chapter 5

Methane Dehydrogenation on Supported Metal Nanoclusters

5.1 Introduction

For practical methane dehydrogenation applications, however, the Pt nanocluster is often deposited onto a specific metal oxide support for use in packed bed reactors, where the support maintains the structural stability of the metal nanoparticle under harsh operating conditions. In some cases, the support itself may also affect the catalytic activity and selectivity of the metal nanocluster, by changing the electronic structure at the metal-metal oxide interface and thus influencing the shape formed by the growing metal nanoclusters and the availability of active sites at sharp corners and edges of these nanoclusters [141, 142, 143, 144, 145, 146, 147, 148, 149]. Several metal oxides have been used as catalytic supports, including magnesia [144], alumina [131], titania [148], zirconia [148], and ceria [130].

Among these various supports, ceria (CeO₂) is attracting increased interest as an active catalyst for oxidation and reduction reactions, due to its high oxygen storage capacity. Ce ably and reversibly converts between Ce⁴⁺ and Ce³⁺ upon release and storage of oxygen [37]. A number of first-principles studies have explored the stoichiometric bulk and associated clean and reduced surfaces[150, 151, 152, 153]. While the (111) surface is more thermodynamically stable, the (110) surface is more catalytically active [154, 155, 156] due to its propensity towards reduction and the formation of oxygen vacancies [157, 158] (i.e., the energy of formation for a single surface oxygen vacancy, with release of \( \frac{1}{2} \) \( \text{O}_2 \), is +2.11 eV on ceria (110) [159] vs. +2.65 eV on ceria (111) [160]).
We aim to better understand the role of a specific support on methane adsorption and dehydrogenation through three sets of systematic studies. First, we model methane adsorption and dehydrogenation ($\text{CH}_3 + \text{H}$) on ceria-supported Pt nanoclusters, and compare to analogous calculations on silica-supported Pt nanoclusters. Then, we postulate reaction paths for methane dehydrogenation on ceria-supported Pt nanoclusters and compute the energies of activation. These studies enable us to develop a molecular understanding of the structure-property relationships that govern catalytic activity and selectivity for methane dehydrogenation at the metal-support interface.

### 5.2 Model and Method

Both silica and ceria are common supports for Pt nanoparticles in catalytic reactions. $\beta$-cristobalite serves as a crystalline phase that is structurally similar to the amorphous silica support, as determined by neutron diffraction. Platinum nanoclusters are modeled in accordance with our published methodology [161]; we investigate the effect of catalyst shape by modeling both a Pt$_{21}$ hemisphere and a Pt$_{20}$ tetrahedron as representation of nanometer-sized clusters. Pt$_{21}$ contains three atomic layers, containing 12, 5, and 4 atoms, respectively; it possesses three types (six in total) of adsorption sites (Figure 5.2): 1. Atop, including the ”vertex”, side atop, and bottom atop (adsorbate binds to only one platinum atom), 2. Bridge, including at the ”vertex” and bottom bridge (adsorbate binds to two adjacent platinum atoms), 3. FCC/HCP (adsorbate binds at the interstice formed by three close-packed platinum atoms). Pt$_{20}$ is a magic cluster [135] that contains four atomic layers, containing 10, 6, 3, and 1 atoms, respectively; it possesses three types (eight in total) of adsorption sites (Figure 5.3): 1. Atop, edge atop, side atop, and bottom vertex (adsorbate binds to only one platinum atom), 2. Bridge, including edge, side, and bottom (adsorbate binds to two adjacent platinum atoms), and 3. FCC/HCP (adsorbate binds at the interstice formed by three close-packed platinum atoms).

Semi-infinite slabs of $\beta$-cristobalite (110) and ceria (110), each containing 5 atomic layers with the bottom three layers constrained in space, serve as the supports for Pt nanoclusters; a $3\times3\times1$ $k$-point mesh, with 15 Å of vacuum between periodic images in the $z$ direction, is used in accordance with our practice [153]. Due to the 1 nm size of the clusters, $p (4 \times 4)$ supercells
of the respective metal oxide supports are used to prevent spurious interactions between neighboring periodic images. The reduced CeO$_{2-x}$ (110) surface is formed by removing one oxygen atom from the topmost atomic layer of the stoichiometric slab and allowing the surface to reconstruct [162, 163, 164, 165, 153]. Optimized $p\,(4 \times 4)$ surface slab models for $\beta$-SiO$_2$ (110), CeO$_2$ (110), and reduced CeO$_{2-x}$ (110) are shown in Figure 5.1.

![Figure 5.1: Top view of optimized support](image)

The number of atoms in the metal-support models is large enough that some atoms must be fixed in space due to computational limitations. The fixed Pt atoms, denoted by yellow stars in Figures 5.2 and 5.3, are located far from the proposed methane adsorption sites and thus not expected to significantly affect the energetics of adsorption. All other Pt atoms are structurally optimized along with the adsorbate molecule(s).

Methane (CH$_4$) and the product of its first carbon-hydrogen bond scission – methyl group (CH$_3$) and hydrogen (H) – are initially placed 2.5 Å above each of the possible adsorption sites on both supported Pt nanoclusters, and then structurally optimized to find the most energetically adsorption configurations and energies. In several cases, the adsorbates migrated from their initial sites to one of the other sites, as will be described in more detail in Section 5.3. We will show that methane adsorbs strongly at the metal-support interface, and thus, since van der Waals interactions are expected to be minor compared to covalent interactions, dispersion corrections are not included in our calculations.

Similar with calculation for dehydrogenation of methane on pure Pt, the PBE functional was used treat the exchange-correlation energy according to the generalized gradient approximation, and the PAW method, with a 400 eV energy cutoff was used to represent the electronic
Figure 5.2: Potential adsorption sites on a hemispherical Pt$_{21}$ nanocluster. All atoms are free to move in space, except for those denoted with yellow stars.

Figure 5.3: Potential adsorption sites on a tetrahedral Pt$_{20}$ nanocluster. All atoms are free to move in space, except for those denoted with yellow stars.
wavefunctions under periodic boundary conditions. All calculations were performed to an energy convergence within $1 \times 10^{-5}$ eV.

The electronic band structure of bulk ceria contains two energy gaps, as determined by XPS spectra: 1. A 3 eV band gap between the O 2$p$ valence band and the Ce 4$f$ conduction band, and 2. A 6 eV band gap between the valence band and the Ce 5$d$ band [166, 167, 168]. Since it is difficult to accurately represent the 4$f$ states in ceria using conventional DFT methods [151, 169, 170], we chose to employ the Hubbard $U$ parameter within the GGA+U approach [171, 172]. The Hubbard $U$ term acts as an on-site Coulombic interaction to properly localize the electrons in these states, which is especially important for the calculations on reduced ceria, with its partially occupied 4$f$ states. We chose for our ceria system $U_{eff} = 5$ eV, which is consistent with recommended values previously published in the literature [173].

To study methane dehydrogenation on the Pt nanoclusters, we used the climbing-image nudged elastic band (CI-NEB) method [47, 136] to locate transition states and calculate the energies of activation and resulting reaction pathways. The initial and final states were located as close as possible to the optimal CH$_3$ + H adsorption site. Four images between the initial and final states were deemed sufficient to direct the system, via force projection, towards the minimum energy pathways for methane dehydrogenation. Since we expect that the scission of the first C-H bond is the rate-limiting step in methane activation, based on our previous studies of methane dehydrogenation on unsupported Pt nanoclusters and literatures [124, 117, 129, 126, 130], we focus here only on this first C-H bond scission step on supported Pt nanoclusters.

### 5.3 Results and Discussion

#### 5.3.1 Adhesion of Pt clusters to supports

We find that a single Pt atom preferentially binds to oxygen vacancy sites of the reduced ceria surface compared to the stoichiometric ceria surface, with the difference of 0.2 eV in the energy of adsorption between the two surfaces. Therefore, we model the Pt$_{21}$/CeO$_{2-x}$ (110) and Pt$_{20}$/CeO$_{2-x}$ (110) systems as shown in Figures 5.4 and 5.5, where the Pt$_{21}$ cluster
is supported stably with its four bottom vertex atoms atop oxygen vacancy sites on the ceria support. Likewise, we position two out of three bottom vertex atoms of the Pt\textsubscript{20} cluster atop the oxygen vacancies on the reduced ceria (110) surface; due to the position of vacancies in the original $p(1 \times 1)$ unit cell, and for consistency with the Pt\textsubscript{21} study, the third bottom vertex atom of the Pt\textsubscript{20} cluster is situated between vacancy sites on the ceria support. For the defect-free silica and stoichiometric ceria surfaces, we place Pt\textsubscript{20} and Pt\textsubscript{21} at the same locations as they are on CeO$_{2-x}$ (110). We do not vary the site of adhesion between the Pt nanocluster and support, not do we consider the addition of oxygen vacancies at the surface, but we propose that future studies could further explore the effect of the metal-support interface structure on catalytic activity and selectivity.

### 5.3.2 CH\textsubscript{4} adsorption on supported Pt nanoclusters

We first present our results on the adsorption of CH\textsubscript{4} to $\beta$-SiO\textsubscript{2}-supported Pt nanoclusters. We find that methane (CH\textsubscript{4}) adsorbs only to three types of atop sites on the $\beta$-SiO\textsubscript{2}-supported Pt\textsubscript{21} hemisphere, since it migrates off of bridge and FCC/HCP sites to adjacent atop sites. The calculated energies of adsorption are $E_{ads} = -0.05$ eV on an atop site, $E_{ads} = -0.08$ eV on a side atop site, and $E_{ads} = -0.07$ eV on a bottom atop site, respectively (Table 5.1); for comparison, the energy of adsorption for CH\textsubscript{4} on Pt (111) is approximately 0 eV, since the interaction with the substrate is mainly due to dispersive forces that are not captured with standard density functional theory calculations [130]. The highest adsorption energy at the side atop site is consistent with our previous result on the unsupported Pt\textsubscript{21} hemisphere ($E_{ads} = -0.10$ eV on an atop site [161]). For the $\beta$-SiO\textsubscript{2}-supported Pt\textsubscript{20} tetrahedron, we find that methane adsorbs preferentially to the atop site, possibly to minimize steric hindrance between the hydrogen atoms of methane and the platinum atoms, with $E_{ads} = -0.19$ eV, (Table 5.2); this value is also consistent with our previous result on the unsupported Pt\textsubscript{20} tetrahedron ($E_{ads} = -0.17$ eV on an atop site [161]). We also observed weak methane adsorption at the edge bridge site and bottom bridge site, where $E_{ads} = -0.05$ eV and $E_{ads} = -0.07$ eV, respectively. To compare the adsorption on the SiO\textsubscript{2}-supported Pt\textsubscript{21} hemisphere and the SiO\textsubscript{2}-supported Pt\textsubscript{20} tetrahedron, we note that the highest adsorption energy of the latter is still roughly twice that calculated on the former; thus, the effect of
the Pt cluster shape still significantly affects the methane adsorption on SiO$_2$-supported Pt nanoclusters, as it does on unsupported Pt nanoclusters.

Since the computed energies of adsorption for methane on supported Pt nanoclusters are very similar to those on the analogous unsupported Pt nanoclusters, we believe that $\beta$-SiO$_2$, due to its role as an inert support, does not significantly affect CH$_4$ adsorption on Pt nanoclusters. Thus, we do not expect any enhancement of catalytic activity for methane dehydrogenation on this support, and will not discuss it further.

We then present our results on the adsorption of CH$_4$ to CeO$_2$-supported Pt nanoclusters. The energies of adsorption presented in Tables 5.1 and 5.2 suggest that both stoichiometric CeO$_2$ and reduced CeO$_{2-x}$ do affect CH$_4$ adsorption to the Pt nanoclusters. (We note that our practice of fixing some Pt atoms in space during the geometry optimization steps does not significantly change, by more than 1.6%, the computed energies of adsorption for CH$_4$ on the supported Pt clusters, since at least 7.0Å separates each fixed Pt atom from the CH$_4$ adsorbate.) No precursor state [174] for CH$_4$ adsorption was found on the ceria-supported Pt cluster, since a second CH$_4$ molecule does not adsorb onto a CH$_4$-occupied adsorption site; this is in accordance with experimental findings on analogous systems [130].

Table 5.1: Energies of adsorption (eV) for CH$_4$ on a hemispherical Pt$_{21}$ nanocluster with different supports. The dash (—) denotes that no adsorption was observed for that particular site, so the molecule migrates to other sites upon structural optimization.

<table>
<thead>
<tr>
<th>Hemispherical Pt$_{21}$ nanocluster</th>
<th>No support</th>
<th>SiO$_2$</th>
<th>CeO$_2$</th>
<th>CeO$_{2-x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>atop</td>
<td>-0.03</td>
<td>-0.05</td>
<td>-0.19</td>
<td>-0.18</td>
</tr>
<tr>
<td>FCC/HCP</td>
<td>—</td>
<td>—</td>
<td>-0.11</td>
<td>-0.07</td>
</tr>
<tr>
<td>side atop</td>
<td>—</td>
<td>-0.08</td>
<td>-0.09</td>
<td>-0.18</td>
</tr>
<tr>
<td>side bridge</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>-0.18</td>
</tr>
<tr>
<td>bottom atop</td>
<td>-0.10</td>
<td>-0.07</td>
<td>-0.18</td>
<td>-0.23(vacancy)/-0.20</td>
</tr>
<tr>
<td>bottom bridge</td>
<td>—</td>
<td>—</td>
<td>-0.14</td>
<td>-0.21(vacancy)/-0.16</td>
</tr>
</tbody>
</table>

In particular, the adsorption of CH$_4$ at the bottom of the nanocluster near the oxygen vacancy on the reduced ceria surface is particularly strong compared to the other adsorption sites. The orientation of the CH$_4$ molecule as it approaches the reduced ceria support suggests that CH$_4$ favors a configuration where one C\textendash{}H bond points towards the bottom atop site on Pt$_{21}$ and the bottom vertex site on Pt$_{20}$, as shown in Figures 5.4 and 5.5. We thus expect
Table 5.2: Energies of adsorption (eV) for CH$_4$ on a tetrahedral Pt$_{20}$ nanocluster with different supports. The dash (—) denotes that no adsorption was observed for that particular site, so the molecule migrates to other sites upon structural optimization.

<table>
<thead>
<tr>
<th>Tetrahedral Pt$_{20}$ nanocluster</th>
<th>No support</th>
<th>SiO$_2$</th>
<th>CeO$_2$</th>
<th>CeO$_{2-x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>atop</td>
<td>-0.17</td>
<td>-0.19</td>
<td>-0.27</td>
<td>-0.29</td>
</tr>
<tr>
<td>edge bridge</td>
<td>-0.02</td>
<td>-0.05</td>
<td>-0.16</td>
<td>-0.15</td>
</tr>
<tr>
<td>edge atop</td>
<td>—</td>
<td>—</td>
<td>-0.12</td>
<td>-0.19</td>
</tr>
<tr>
<td>FCC/HCP</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>-0.07</td>
</tr>
<tr>
<td>side atop</td>
<td>-0.02</td>
<td>-0.01</td>
<td>-0.19</td>
<td>-0.17</td>
</tr>
<tr>
<td>side bridge</td>
<td>—</td>
<td>—</td>
<td>-0.13</td>
<td>—</td>
</tr>
<tr>
<td>bottom vertex</td>
<td>-0.17</td>
<td>-0.08</td>
<td>-0.19</td>
<td>-0.37(vacancy)/-0.25</td>
</tr>
<tr>
<td>bottom bridge</td>
<td>-0.02</td>
<td>-0.07</td>
<td>-0.18</td>
<td>-0.31(vacancy)/-0.22</td>
</tr>
</tbody>
</table>

Rotational steering forces to drive CH$_4$ into the favorable orientations near the surface oxygen vacancy during our subsequent dissociative chemisorption studies of CH$_3$ on Pt$_{21}$ or Pt$_{20}$, as will be described later in this section.

We conclude that oxygen vacancies at the surface of the ceria support play an important role in enhancing the strength of CH$_4$ adsorption on Pt nanoclusters. For Pt nanoclusters supported on stoichiometric ceria, the strongest adsorption sites are atop the cluster, near the vertex and away from the support. However, Pt nanoclusters supported on reduced ceria prefer to adsorb at bottom atop or bottom vertex sites nearest the surface oxygen vacancy. We thus further explore whether these structure-property relationships correlate to catalytic activity for methane dehydrogenation.

### 5.3.3 CH$_3$ + H dissociative chemisorption on supported Pt nanoclusters

We now present our results on the adsorption of CH$_3$ + H to reduced ceria-supported Pt nanoclusters in Tables 5.3 and 5.4. On hemispherical Pt$_{21}$, CH$_3$ is chemisorbed to the side atop site, with symmetric $d$(Pt−C) = 2.214 Å and $d$(C−H) = 1.125 Å. The dissociated H atom chemisorbs to the oxygen vacancy site on reduced ceria, such that $d$(O$_v$−H) = 1.604 Å.
Figure 5.4: CH$_4$ adsorption on reduced ceria supported Pt$_{21}$

Table 5.3: Energies of adsorption (eV) for CH$_3$ + H on a hemispherical Pt$_{21}$ nanocluster with reduced ceria support. The dash (—) denotes that no adsorption was observed for that particular site, so the molecule migrates to other sites upon structural optimization.

<table>
<thead>
<tr>
<th>H chemisorption site</th>
<th>CH$_3$ chemisorption site</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bottom atop</td>
<td>bottom bridge</td>
<td>side atop</td>
<td>side bridge</td>
<td>O$_\nu$ (ceria surface)</td>
</tr>
<tr>
<td>bottom atop</td>
<td>—</td>
<td>-3.89</td>
<td>-3.97</td>
<td>—</td>
<td>-2.91</td>
</tr>
<tr>
<td>bottom bridge</td>
<td>-4.08</td>
<td>—</td>
<td>-3.97</td>
<td>-3.87</td>
<td>-2.95</td>
</tr>
<tr>
<td>side atop</td>
<td>—</td>
<td>-4.10</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>side bridge</td>
<td>-4.02</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>-2.90</td>
</tr>
<tr>
<td>O$_\nu$ (ceria surface)</td>
<td>-4.07</td>
<td>-4.09</td>
<td>-4.23</td>
<td>-4.12</td>
<td>—</td>
</tr>
</tbody>
</table>
Table 5.4: Energies of adsorption (eV) for CH$_3$ + H on a tetrahedral Pt$_{20}$ nanocluster with reduced ceria support. The dash (—) denotes that no adsorption was observed for that particular site, so the molecule migrates to other sites upon structural optimization.

<table>
<thead>
<tr>
<th>H chemisorption site</th>
<th>CH$_3$ chemisorption site</th>
<th>O$_v$ (ceria surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bottom vertex</td>
<td>bottom bridge</td>
</tr>
<tr>
<td>bottom vertex</td>
<td>—</td>
<td>-3.90</td>
</tr>
<tr>
<td>bottom bridge</td>
<td>-4.01</td>
<td>—</td>
</tr>
<tr>
<td>edge atop</td>
<td>-3.91</td>
<td>-4.025</td>
</tr>
<tr>
<td>edge bridge</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>O$_v$ (ceria surface)</td>
<td>-4.12</td>
<td>-4.01</td>
</tr>
</tbody>
</table>
The total energy of adsorption for both CH$_3$ and H to Pt$_{21}$ is $E_{ads} = -4.23$ eV, as summarized in Figure 5.6. If only CH$_3$ is chemisorbed at the same side atop site, the adsorption energy is $-2.08$ eV, with $d$(Pt–C) = 2.205 Å; note that the adsorption energy on the Pt (111) surface is roughly -(1.93-2.04) eV [175, 176]. If only H is chemisorbed at the same oxygen vacancy site, the adsorption energy is $-2.79$ eV, with $d$(O$_v$–H) = 1.665 Å. Thus, when CH$_3$ and H coadsorb to Pt$_{21}$/CeO$_{2-x}$, the calculated energy of adsorption is 0.64 eV less than the sum of the adsorption energies from CH$_3$ and H chemisorbed separately (-4.87 eV); this suggests a weakly competitive co-adsorption, upon which the Pt–C distance increases slightly but the O$_v$–H distance decreases compared to adsorption of the individual molecules.

On tetrahedral Pt$_{20}$, CH$_3$ is chemisorbed to the edge bridge site, with symmetric $d$(Pt–C) = 2.113 Å and and $d$(C–H) = 1.109 Å. The dissociated H atom chemisorbs to the oxygen vacancy site on reduced ceria, such that $d$(O$_v$–H) = 1.601 Å.

The total energy of adsorption for both CH$_3$ and H to Pt$_{20}$ is $-4.37$ eV, as summarized in 5.6. If only CH$_3$ is chemisorbed at the same side atop site, the adsorption energy is $-2.19$ eV, with asymmetric $d$(Pt–C) = 2.095 – 2.102 Å. If only H is chemisorbed at the same oxygen vacancy site, the adsorption energy is $2.76$ eV, with $d$(O$_v$–H) = 1.637 Å. Thus, when CH$_3$ and H coadsorb to Pt$_{20}$/CeO$_{2-x}$, the calculated energy of adsorption is 0.58 eV less than the sum of the adsorption energies from CH$_3$ and H chemisorbed separately (-4.95 eV).

We conclude that CH$_3$ prefers to adsorb to the Pt nanocluster and H prefers to absorb to the O$_v$ vacancy site on the ceria surface. While CH$_3$ prefers the side atop site of hemispherical Pt$_{21}$ and the edge bridge site of tetrahedral Pt$_{20}$, in accordance with the results on unsupported Pt nanoclusters [161], both nanoclusters induce weakly competitive co-adsorption behavior for CH$_3$ + H. Nevertheless, the overall energetics are favorable for the methane dehydrogenation reaction.

5.3.4 Methane dehydrogenation pathway

Finally, we analyze the energy barriers to reaction that ultimately help us understand the catalytic role of the metal-support interface. We focus our calculations and analyses on the first dehydrogenation of methane, which has been proposed as the rate-limiting step and
Figure 5.6: CH$_3$*+H* chemisorption on Pt$_{21}$/CeO$_{2-x}$

\[ E_{\text{ad}} = -4.23 \text{eV} \]
\[ d_{C-Pt} = 2.214 \text{Å} \]
\[ d_{H-O_v} = 1.604 \text{Å} \]
\[ \angle_{\text{HCH}} = 106.7^\circ \]

(a) CH$_3$*+H* chemisorption on Pt$_{21}$/CeO$_{2-x}$

\[ E_{\text{ad}} = -4.37 \text{eV} \]
\[ d_{C-Pt} = 2.113 \text{Å} \]
\[ d_{H-O_v} = 1.601 \text{Å} \]
\[ \angle_{\text{HCH}} = 105.9^\circ \]

(b) CH$_3$*+H* chemisorption on Pt$_{20}$/CeO$_{2-x}$

Figure 5.6: CH$_3$+H chemisorption on reduced ceria supported Pt nanoclusters
supported by our previous studies and others in the published literature [124, 117, 129, 126, 130, 161].

The computed energy profiles, including energies of activation, are shown in Figures 5.7 and 5.8. We see a pronounced effect of the reduced ceria support on the energy barrier for the first C–H bond scission in methane, compared to that on the unsupported Pt nanocluster. The reduced ceria support decreases the energy barrier by 0.06 eV on Pt	extsubscript{21} and 0.15 eV on Pt	extsubscript{20}, compared to the corresponding unsupported Pt clusters. For reference, the calculated vibrational zero-point energy (ZPE) corrected activation barrier for the first C–H bond scission of methane on Pt	extsubscript{21}/CeO	extsubscript{2-x} is 0.304 eV, which is slightly smaller than non-ZPE-corrected value of 0.331 eV; a similar reduction in $E_a$ from 0.390 eV to 0.359 eV is observed on unsupported Pt when the ZPE correction is applied. Thus, since C–H bonds vibrate at higher frequencies than Pt–H bonds, inclusion of ZPE effects is not expected to significantly affect the mechanistic pathways and our main conclusion on the effect of metal-support interactions on methane dehydrogenation – that the reduction in the energy barrier to C–H bond activation may be primarily attributable to the compressive strain [177] (e.g., at the bottom vertex sites of the supported Pt nanoclusters closest to the surface oxygen vacancies, the Pt–Pt distances are $\approx$ 0.1 Å shorter than those in the unsupported nanoclusters) and corresponding increase in electron density and catalytic activity, for the ceria-supported Pt nanocluster.

For comparison of our energy profiles in Figures 5.7 and 5.8 to published results, we provide a brief literature survey of the initial C–H dehydrogenation step for CH₄ on a Pt slab, ceria slab, and or/ Pt-doped ceria slab. Chen and Vlachos [178] studied methane dehydrogenation on Pt (111), and found that the dissociating hydrogen atom was preferentially located near an atop position in the transition-state geometry, and the methyl fragment was located close to a site determined by the valency of the fragment; the computed energy of activation for the first C–H bond activation was 0.63 eV, which is consistent with that obtained by Michaelides et al. [179], but smaller than the 0.9 eV barrier obtained by Viñes et al. [130]. Both Petersen et al. and Moussounda et al. located the lowest-energy transition state for methane dehydrogenation on Pt (110), and found that the C–H bond dissociation occurred on the close-packed Pt ridge, resulting in CH₃ chemisorbed to the ridge atop site step; the calculated energy barrier to activation ranges from 0.35 eV [139] to 0.53 eV [180]. Liu et al. extended this discussion on CH₄ dehydrogenation to stepped and stepped-kinked Pt surfaces.
Figure 5.7: Energy profiles for methane dehydrogenation from CH$_4$ to CH$_3$ + H on hemispherical Pt$_{21}$ and Pt$_{21}$/CeO$_{2-x}$. 
Figure 5.8: Energy profiles for methane dehydrogenation from CH$_4$ to CH$_3$ + H on tetrahedral Pt$_{20}$ and Pt$_{20}$/CeO$_{2-x}$.

Reaction Coordinates
the energy barrier for C–H dehydrogenation on Pt (211) is 0.21 eV [178]. Finally, Tang et al. computed the energy barrier for C–H cleavage as 1.29 eV on pure ceria and 1.08 eV on Pt-doped ceria [182]. Our computed energy barriers on reduced ceria-supported Pt clusters (0.24-0.33 eV) are lower than any of the discussed alternative catalysts systems. This suggests that a reduced ceria support, with the corresponding surface oxygen vacancy, greatly enhances the activity of (111)-facing Pt clusters to match or exceed the activity of the stepped (211) surface, and the role of catalyst shape should be the subject of increased interest in when designing catalysts for methane C–H bond activation and cleavage.

The ceria support effect also results in a slight difference in the energies of reaction. For the unsupported Pt nanoclusters, methane dehydrogenation is exothermic. For the reduced ceria-supported Pt nanoclusters, methane dehydrogenation appears to be slightly endothermic. The comparison is not direct, as the dissociated H atom binds not to the Pt cluster but rather to the ceria support, as would be expected following H migration to the reduced Ce surface ions near the oxygen vacancy. While the support and associated compressive strain are highly important for lowering the energy barrier for activating and cleaving the first C–H bond of methane, the Pt nanocluster shape is still important in dictating the energies of reaction. The edges and vertices of the tetrahedral Pt$_{20}$ nanocluster, with their increased electron density [161], improve upon both the energy barrier to CH$_4$ activation and energy of adsorption for CH$_3$. Furthermore, the support stabilizes methane and its hydrogenated derivatives a bit more on tetrahedral Pt$_{20}$ compared to hemispherical Pt$_{21}$, so the stabilized CH$_3$ may serve as the building block towards the production of chemicals and fuels.

5.4 Summary

We have investigated the energetics of methane adsorption and the first C–H bond scission step on nanometer-sized Pt clusters supported on ceria (110), using density functional theory with Hubbard $U$ corrections for the Ce 4$f$ states, and compared our results to analogous calculations on $\beta$-cristobalite (110). There is no significant enhancement in the energy of adsorption for methane on Pt/$\beta$-cristobalite (110) compared to unsupported Pt. However, Pt/ceria (110) does significantly enhance methane adsorption, and we note a significant effect of chemical composition of the support; on the stoichiometric ceria (110) support, methane
prefers to adsorb atop the vertex of the Pt cluster and away from the support, much like it does on the unsupported Pt, but on the reduced ceria (110) support, methane instead prefers to adsorb atop the Pt atoms nearest the oxygen vacancies at the metal-support interface. Following methane dehydrogenation, CH$_3$ prefers to adsorb to the Pt nanocluster and H prefers to absorb to the oxygen vacancy site on the ceria surface. The reduced ceria (110) support significantly lowers the energy barrier of dehydrogenation on Pt nanoclusters, compared to the unsupported Pt nanoclusters. We propose that several structure-property relationships in catalyst shape and composition, including the increased electron density and compressive strain at low-coordinated Pt sites and oxygen vacancies at the metal-support interface all contribute cooperatively to the enhanced catalytic activity. Furthermore, the reduced ceria support stabilizes methane and its hydrogenated derivatives, so CH$_3$ may serve as the building block towards the production of chemicals and fuels. Our results confirm the critical role of support structure and composition for catalytic methane activation and dehydrogenation on noble metal clusters.
Chapter 6

C–O Bond Activation on Reducible Metal Oxides

6.1 Introduction

The synthesis of liquid fuels and commodity chemicals from carbon dioxide (CO$_2$) is a promising approach for clean energy production. For this reason, much academic and industrial effort has been devoted to exploring efficient means of reducing CO$_2$ [183]. It is widely believed that the first step in CO$_2$ reduction is the activation of the C=O bond and charge transfer for the eventual formation of an anion radical species. Since CO$_2$ is thermodynamically stable and the formation of the radical is difficult in the gas phase [28], we seek appropriate catalysts for lowering the activation barrier to (photo)electrochemical CO$_2$ reduction.

There have been several metal oxides proposed for CO$_2$ activation, such as ZrO$_2$ [30], TiO$_2$ [31, 32, 33, 34], MgO [35], and CaO [36]. Among these various catalysts for CO$_2$ activation, ceria (CeO$_2$) is attracting increased interest due to its high oxygen storage capacity. Ceria is commonly used for oxidation and reduction reactions, since Ce ably and reversibly converts between Ce$^{4+}$ and Ce$^{3+}$ upon release and storage of oxygen [37].

A number of first-principles studies on ceria have confirmed the structure and properties of the stoichiometric bulk and associated surfaces. Reduced ceria surfaces that contain oxygen vacancies have also been studied extensively [150, 151, 184, 152]. In this work, we focus on the ceria (110) surface, for which the stoichiometric repeating unit consists of two oxygen
anions and two cerium cations that are bonded in a diamond configuration and to other repeating units. While the ordering of the thermodynamic stability of ceria surfaces is (111) > (110) > (100) [154, 155, 156], and the majority of the it is believed that the metastable ceria (110) surface is more catalytically active than either the (111) or the (100) surfaces, since the creation of oxygen vacancies on the ceria (110) surface requires the least amount of energy [157, 158, 160, 159]. Thus, the ceria (110) surface appears to be the most promising candidate for catalyzing reactions that involve oxygen cycling with the adsorbates, so we focus on this low-index surface for carbon dioxide reduction.

Naturally, the formation of surface oxygen vacancies is key to the success of the proposed catalytic reaction. Two types of vacancies have been reported on the ceria (110) surface: 1. In-plane vacancy structure, and 2. Split vacancy structure. From the baseline repeating unit, the in-plane vacancy structure simply has one of the surface oxygen anions removed, and little surface reconstruction is observed; this structure has been confirmed using density functional theory (DFT) calculations [185, 159]. The split vacancy structure, however, exhibits significant in-plane and out-of-plane movement of the remaining surface oxygen anion (O\text{v}), so that it bridges the surface cerium cations and is situated above the topmost atomic layer; this structure has also been confirmed by DFT calculations [157, 158, 186], embedded cluster calculations with many-body perturbation theory [155], and potential-based molecular dynamics simulations [187]. The split vacancy structure has also been observed for metal-doped ceria (110) surfaces [188]. Since these two vacancy structures are quite different, CO\textsubscript{2} adsorption, and eventually reduction, at these sites may follow different pathways. Thus, carbon dioxide reduction at both types of surface vacancies should be considered to understand the effect of catalyst structure on reactivity [189, 190, 191, 156, 192].

In particular, we are interested in determining whether carbon dioxide necessarily follows the simple dissociation to form carbon monoxide (CO) and ”heal” the surface vacancy on the reduced ceria (110) surface, or whether it may follow a different reduction pathway. The ”reverse” of this process, namely, CO oxidation on stoichiometric ceria [191, 193, 194, 195, 196], has been well-studied for a range of applications, including three-way automotive catalysts (TWC), the water-gas shift (WGS) reaction [197, 198], and syngas production [199, 200]. However, CO\textsubscript{2} reactivity remains ambiguous, since neither theoretical or experimental studies have clarified the exact mechanism of CO\textsubscript{2} activation nor the structure of the adsorbed species on the ceria (110) surface. A recent x-ray photoemission spectroscopy (XPS) study
supports the hypotheses that CO$_2$ activation may involve formation of surface carboxylates, and the degree of carbonate formation may not be directly related to the surface re-oxidation process [201]. Another recent resonant photoemission spectroscopy (RPES) study suggests that partial re-oxidation of reduced ceria occurs with high reaction probability, so that further clarification of CO$_2$ activation and surface re-oxidation is necessary [202].

We now present three sets of theoretical and computational studies that aim to provide a mechanistic understanding of CO$_2$ activation and reduction on ceria (110) surfaces. First, we demonstrate the formation of the in-plane and split vacancies on the ceria (110) surface, and quantify the resulting structures and energetics. Second, we quantify the adsorption and electronic properties, including charge transfer, for CO$_2$ on the stoichiometric ceria (110) surface, reduced (in-plane vacancy) ceria (110) surface, and reduced (split vacancy) ceria (110) surface. Third, we map out reaction pathways for CO$_2$ dissociation to CO, with accompanying energies of activation, at the in-plane and split vacancies. Our results provide detailed theoretical evidence that reduced ceria surfaces induce CO$_2$ activation to form carbonate anions, but the nature of these carbonates depends on the geometry of the vacancy site; thus, the mechanism and energetics of CO$_2$ dissociation depends greatly on the structure and properties of the catalyst surface, so that it cannot be always considered as the reverse of CO oxidation on the stoichiometric ceria catalyst.

### 6.2 Model and Method

We still used 400 eV as energy cutoff to describe the wavefunctions of the atomic cores, and tetrahedron method with Bl"ochl corrections to set the partial occupancies for the orbitals. While several $k$-point mesh sizes (e.g. $4 \times 4 \times 4$ up to $11 \times 11 \times 11$) were considered, we ultimately used the $6 \times 6 \times 6$ $\Gamma$-centered Monkhorst-Pack $k$-point mesh for bulk ceria to give results that were sufficiently converged within $1 \times 10^{-5}$ eV, using the conjugate gradient method. Because of the $4f$ states in ceria we still chose to employ the Hubbard $U$ parameter within the GGA+U ($U_{eff} = 5$ eV) approach.

The bulk ceria unit cell contains 8 oxygen atoms and 4 cerium atoms in a cubic unit cell with the $Fm\bar{3}m$ symmetry space group; the initial lattice parameter is $|a| = 5.411$ Å [203]. After GGA+U geometry optimization, the bulk lattice parameter increased slightly to $|a|$ =
5.413 Å; this compares favorably to previous studies that also follow the DFT approach [204] as well as the bulk lattice parameter of $|\mathbf{a}| = 5.482$ Å obtained using pure GGA. For comparison, we note that the use of $U_{\text{eff}} = 3$ eV gives $|\mathbf{a}| = 5.478$ Å, and $U_{\text{eff}} = 7$ eV gives $|\mathbf{a}| = 5.381$ Å. Thus, $U_{\text{eff}} = 5$ eV is used in all subsequent calculations.

Semi-infinite slab models, consisting of 10 atomic layers and 15 Å of vacuum between periodic images in the $z$ direction, were cleaved along the (110) plane from the optimized bulk ceria unit cell; following optimization, we observed that atomic layer relaxation occurred primarily within the three topmost layers. Thus, we cleaved the slab in half along the $xy$ plane, so that the slab consisting of 5 atomic layers (overall slab thickness is 7.622 Å), with the bottom two layers constrained in space, was used for all subsequent calculations. The other atoms were free to move in all directions within the fixed lattice. A $p (2 \times 2)$ supercell, with a corresponding $3 \times 3 \times 1$ $k$-point mesh, is used in accordance with the practice adopted by other researchers studying the adsorption of small molecules on the ceria (110) surface [205, 206, 207]. We believe that the exposed surface area is large enough to accommodate a small gas-phase adsorbate (e.g., CO$_2$) without spurious interactions from neighboring images, as we will show in Section 6.3.

The energy of adsorption for carbon dioxide on ceria is given as:

$$E_{\text{ads}} = E_{\text{CO}_2+\text{CeO}_2(110)} - E_{\text{CeO}_2(110)} - E_{\text{CO}_2}$$

where $E_{\text{CeO}_2(110)}$ is the total energy of the ceria (110) surface slab, $E_{\text{CO}_2}$ is the total energy of the CO$_2$ molecule (optimized in a periodic cubic unit cell whose volume is 8000 Å$^3$), and $E_{\text{CO}_2+\text{CeO}_2(110)}$ is the total energy of the composite system. Since the calculations were performed at 0 K and fixed cell volume, the differences in Gibbs free energy should equal the differences in total energy. By this definition, a negative value of $E_{\text{ads}}$ corresponds to an exothermic and spontaneous adsorption process.

Since the clean ceria (110) surface is atomically flat, both parallel and perpendicular/vertical orientations of CO$_2$ were chosen for analysis and comparison, and the energies of adsorption were calculated for each orientation on the stoichiometric and reduced surfaces. The excess spin densities and Bader charges [208] were also calculated to lend insight into the role of charge transfer in CO$_2$ adsorption and activation on the ceria (110) surface.
By including four images between the initial and final states, the CI-NEB method was able to successfully drive the highest energy image up to the exact saddle point and yield accurate minimum energy paths for CO$_2$ dissociation to CO.

6.3 Results and Discussion

The stoichiometric ceria (110) surface contains several distinct sites, including: 1. Threefold coordinated O atoms in the topmost atomic layer (nO), 2. Fourfold coordinated O atoms in the subsurface atomic layer (nnO), 3. Sixfold coordinated Ce atoms in the topmost atomic layer (nCe), 4. Eightfold coordinated Ce atoms in the subsurface atomic layer (nnCe), and 5. Hollow. The reduced ceria (110) surface contains similar sites, except that nCe and nnCe denote fivefold coordinated Ce atoms in the topmost atomic layer and sevenfold coordinated Ce atoms in the subsurface atomic layer, respectively (Figure 6.1). This nomenclature will be used throughout to describe changes in the adsorption configuration and electronic structure at the surface.

![Schematic representations of the stoichiometric and reduced ceria (110) surfaces. Red spheres refer to O atoms and beige spheres refer to Ce atoms.](image)

**Figure 6.1:** Schematic representations of the stoichiometric and reduced ceria (110) surfaces. Red spheres refer to O atoms and beige spheres refer to Ce atoms.

6.3.1 Oxygen Vacancy Formation on Ceria (110)

As stated in Section 6.1, two distinct types of oxygen vacancy sites, in-plane and split, may form on the reduced ceria (110) surface. In this work, only a single oxygen vacancy per $p(2 \times 2)$ supercell was considered to isolate its effect on CO$_2$ activation. For the in-plane vacancy structure, the nO anion nearest the vacancy site moves slightly in-plane towards...
the vacancy. The resulting Ce-O distances are 2.28-2.29 Å, compared to 2.34 Å in the stoichiometric surface. The nCe cations also relax only slightly away from the vacancy, so that the nnCe-nnO distances are 2.31 Å.

For the split vacancy structure, the nO anion nearest the vacancy site moves to fill the vacancy, so that nO is almost equidistant between two nCe atoms; it also moves out of the surface plane in the perpendicular direction. Furthermore, the other nnO and nnCe atoms near the vacancy move slightly away (0.07-0.09 Å) from the vacancy, so that the vacancy site, although split, is still quite large in area and volume. As a result, the average nnCe-nnO distances near the vacancy site increases to 2.35 Å, compared to 2.27 Å in stoichiometric ceria (110). This surface reconstruction in reduced ceria (110) is in agreement with results previously reported in the literature [162, 163, 164, 165].

To compare the stability of these two reduced surfaces, we calculate the vacancy formation energy. We find that the split vacancy structure is slightly more energetically stable, with a vacancy formation energy of +1.651 eV, compared to the in-plane vacancy structure, with a vacancy formation energy of +1.962 eV (Figure 6.2). Our results are comparable to the previously reported split vacancy formation energy of +1.61 eV [186] and in-plane vacancy formation energy of +1.99 eV [185, 209]. Furthermore, an increase in supercell size from $p(2 \times 2)$ to $p(3 \times 3)$ does not affect the geometric structure (i.e., Ce-O distances) and only decreases the vacancy formation energy by 2.3%; thus, the $p(2 \times 2)$ supercell is sufficient for the ensuing analysis.

6.3.2 CO$_2$ Adsorption on Stoichiometric and Reduced Ceria (110)

We now present structures and energies of adsorption for CO$_2$ on the stoichiometric and reduced ceria (110) surfaces.
Figure 6.2: Red lines refer to the energy required to form the oxygen vacancy on the stoichiometric ceria (110) surface, and blue lines refer to the energetic stability of the reduced surface.
CO$_2$ Adsorption on Stoichiometric Ceria (110)

On stoichiometric ceria (110), seven configurations where CO$_2$ is adsorbed parallel to the surface (along either the $x$- or $y$-axis) and four configurations where CO$_2$ is adsorbed perpendicular/vertical to the surface are considered (Figure 6.3). The energies of adsorption, select geometrical parameters, and variation of the total Bader charge of the adsorbed CO$_2$ molecule, following geometry optimization to local minima, are shown in Table 6.1.

![Figure 6.3: CO$_2$ adsorption on $p\,(2\times2)$ supercell of stoichiometric ceria (110). Sp denotes adsorption parallel to the surface, and Sv denotes adsorption perpendicular/vertical to the surface. For the CO$_2$ adsorbate, oxygen is represented by an orange sphere and carbon is represented by a black sphere.](image)

The strongest energy of adsorption ($E_{ads} = -0.262$ eV) is observed for nnO adsorbing as a "bridge" between two nCe atoms (Sp5). The two C-O bonds in CO$_2$ are slightly elongated to 1.196 Å and 1.207 Å, compared to 1.176 Å in the gas phase. The CO$_2$ molecule are nearly linear, with a O-C-O angle of 178.2°. The two oxygen atoms in CO$_2$ reside at the top of two sixfold coordinated surface nCe atoms, and the Ce-O distances are 2.520 Å and 2.527 Å, respectively. An additional depiction of this adsorption configuration (Sp5) is shown in Figure 6.4.
Table 6.1: Representative structural parameters, energies of adsorption, and variation of the total Bader charge for a CO$_2$ molecule adsorbed at various sites (Figure 6.3) on the stoichiometric ceria (110) surface

|     | $r_{C-O}$ (Å) | $\angle O-C-O$ (°) | $E_{ads}$ (eV) | $\Delta \rho (CO_2)_{|e|}$ |
|-----|---------------|-------------------|---------------|---------------------|
| Sp1 | 1.177-1.178   | 180               | -0.034        | -0.003              |
| Sp2 | 1.182-1.185   | 178.8             | -0.118        | -0.002              |
| Sp3 | 1.183-1.186   | 179.2             | -0.183        | -0.005              |
| Sp4 | 1.178-1.182   | 180               | -0.078        | -0.005              |
| Sp5 | 1.196-1.207   | 178.2             | -0.262        | -0.008              |
| Sp6 | 1.180-1.182   | 179.5             | -0.043        | -0.002              |
| Sp7 | 1.179-1.183   | 178.1             | -0.174        | -0.002              |
| Sv1 | 1.172-1.180   | 178.2             | -0.201        | -0.006              |
| Sv2 | 1.173-1.178   | 179.1             | -0.102        | -0.003              |
| Sv3 | 1.175-1.176   | 180               | -0.035        | -0.001              |
| Sv4 | 1.172-1.179   | 180               | -0.253        | -0.003              |

Figure 6.4: CO$_2$ adsorption on stoichiometric ceria (110) in selected configurations: Sp5, Sv4, and Sv1. Both structural parameters and energies of adsorption are depicted.
The Sv4 and Sv1 adsorption configurations are in vertical orientation and tilted slightly relative to the surface normal, yet are slightly less energetically favorable than Sp5 ($E_{ads} = -0.253$ eV and $E_{ads} = -0.201$ eV, respectively). For Sv4, the CO2 adsors at the nnO_nnO hollow site, which is flanked by two subsurface ceria atoms (nnCe) and two subsurface oxygen atoms (nnO). The distance between the ceria surface and the adsorbing oxygen atom in CO2 is 2.631 Å. For Sv1, the CO2 adsors at the nO_nO hollow site, which is flanked by two surface ceria atoms (nCe) and two surface oxygen atoms (nO). The distance between the ceria surface and the adsorbing oxygen atom in CO2 is 2.573 Å. The symmetry of these two hollow sites reduces the net intermolecular forces acting on the CO2 molecule, so these adsorption configurations are relatively stable. However, the lengths of the two C-O bonds in CO2 for the Sv4 and Sv1 configurations are similar to those in gas-phase CO2. Additional depictions of these two adsorption configurations are shown in Figure 6.4.

Several other adsorption configurations merit discussion, in terms of alignment of the adsorbate and consideration of surface/subsurface effects. For Sp1 and Sp4, the C atom of CO2 resides on top of the surface nO atom, but is aligned along different axes ($x$ and $y$, respectively). Both Sp1 and Sp4 result in very weak physisorption, with Sp4 being slightly favored energetically due to the increased electrostatic repulsion with the neighboring surface nO oxygen in the Sp1 configuration compared to the repulsion with the subsurface nnO oxygens in the Sp4 configuration. For Sp2 and Sv2, where CO2 is adsorbed on top of the surface nCe atom, the energy of adsorption is stronger than that for Sp6 and Sv3, respectively, where CO2 is adsorbed on top of the subsurface nnCe atom. Any differences in electrostatic repulsion with subsurface nnCe or nO atoms appear to be minimal, as the energies of adsorption for the Sp3 and Sp7 configurations are nearly identical. Thus, we propose that only surface atoms appear to significantly influence the strength of CO2 adsorption to the stoichiometric ceria (110) surface.

In general, all of these adsorption configurations on stoichiometric ceria (110) would be classified as weak physisorption, since the CO2 molecule remains physically unchanged upon adsorption and the distance between CO2 and the surface is more than 2.52 Å, which is too far to form a Ce-O bond. Furthermore, the Bader charge analysis indicates that the variation of the total charge of adsorbed CO2 is less than $-0.01 |e|$, so there is no significant change in the electronic structure. We can conclude that stoichiometric ceria (110) does not activate the CO2 molecule.
CO$_2$ Adsorption on Reduced (In-Plane Vacancy) Ceria (110)

For reduced ceria (110) with an in-plane vacancy, we only considered CO$_2$ adsorption at the vacancy, since the remainder of the surface is structurally identical to stoichiometric ceria (110) due to the lack of surface reconstruction. We found that the most stable configuration is Rv(InP), as shown in Figure 6.5, with an energy of adsorption of -1.043 eV. For this configuration, one O atom of the CO$_2$ molecule is bound to a surface fivefold coordinated nCe atom that neighbors the vacancy site, and the C atom of the CO$_2$ molecule is bound to the other surface fivefold coordinated nCe atom. This structure, while slightly distorted, would be analogous to the bridged carbonate, formed by CO adsorption to the stoichiometric ceria (110) surface, reported in the literature [191, 193, 196].

![Figure 6.5](image)

Figure 6.5: The most stable CO$_2$ adsorption configuration on reduced ceria (110) with in-plane vacancy (Rv(InP)) and split vacancy (Rp5). The surface oxygen nearest the vacancy is labeled as O$_{v}$. Both structural parameters and energies of adsorption are depicted.

The C atom of the CO$_2$ molecule does not bind to the nO surface oxygen atom neighboring the vacancy in this initial adsorption step, since the oxygen atom is already coordinatively saturated. Instead, it appears to associate with the nearby cerium atoms, so that the Ce-C distance of 1.573 Å is much smaller than the Ce-O distance of 2.011 Å between the surface and adsorbate in the Rv(InP) configuration. The adsorbed CO$_2$ molecule exhibits a bent configuration, where the O-C-O angle is 140.1°. The two C-O bonds are, however,
asymmetrically elongated compared to their values in the gas phase molecule; the C-O bond near the surface increases in length to 1.302 Å, which is about 0.1 Å longer than the other C-O bond length of 1.214 Å in the adsorbed CO$_2$ molecule. We can denote this adsorption structure as an inorganic carboxylate, which has been reported in experimental studies [189]. The energy of adsorption for the Rv(InP) configuration is -1.043 eV, so the interaction of CO$_2$ with the in-plane vacancy may be classified as chemisorption.

**CO$_2$ Adsorption on Reduced (Split Vacancy) Ceria (110)**

The optimized adsorption configurations of CO$_2$ on reduced ceria (110), with a split vacancy, are shown in Figure 6.6. Seven configurations where CO$_2$ is adsorbed parallel to the surface (along either the x- or y-axis) and four configurations where CO$_2$ is adsorbed perpendicular/vertical to the surface were considered. The energies of adsorption, select geometrical parameters, and variation of the total Bader charge of the adsorbed CO$_2$ molecule, following geometry optimization to local minima, are shown in Table 6.2.

Table 6.2: Representative structural parameters, energies of adsorption, and variation of the total Bader charge for a CO$_2$ molecule adsorbed at various sites (Figure 6.6) on the reduced ceria (110) surface with split vacancy

|  | $r_{C-O}$ (Å) | $\theta_{O-C-O}$ (°) | $E_{ads}$ (eV) | $\Delta \rho$(CO$_2$) | $|e|$ |
|---|---|---|---|---|---|
| Rp1 | 1.176-1.183 | 178.3 | -0.401 | -0.273 |
| Rp2 | 1.182-1.197 | 135.5 | -0.119 | -0.223 |
| Rp3 | 1.207-1.287 | 177.3 | -0.201 | -0.119 |
| Rp4 | 1.198-1.311 | 140.4 | -1.012 | -0.936 |
| Rp5 | 1.246-1.256 | 136.9 | -1.223 | -0.955 |
| Rp6 | 1.179-1.183 | 180 | -0.055 | -0.016 |
| Rp7 | 1.177-1.182 | 178.9 | -0.177 | -0.059 |
| Rv1 | 1.168-1.182 | 177.1 | -0.815 | -0.081 |
| Rv2 | 1.201-1.322 | 139.9 | -0.265 | -0.921 |
| Rv3 | 1.172-1.181 | 179.1 | -0.038 | -0.043 |
| Rv4 | 1.175-1.182 | 178.5 | -0.282 | -0.178 |

The strongest energy of adsorption ($E_{ads} = -1.233$ eV) is observed for CO$_2$ parallel adsorption as a "bridge" between two nCe atoms (Rp5) adjacent to the vacancy site. From Figure 6.6, we can see the carbon atom of the adsorbate is situated directly above the nO atom.
Figure 6.6: CO$_2$ adsorption on $p$ ($2 \times 2$) supercell of reduced ceria (110 with split vacancy). Rp denotes adsorption parallel to the surface, and Rv denotes adsorption perpendicular/vertical to the surface. For the CO$_2$ adsorbate, oxygen is represented by an orange sphere and carbon is represented by a black sphere.
that had moved toward the vacancy oxygen atom. Furthermore, the adsorbed CO$_2$ molecule exhibits a bent configuration, where the O-C-O angle is 136.9°. Also, the two C-O bonds in the adsorbed CO$_2$ molecule are elongated (almost) symmetrically to 1.246 Å and 1.256 Å, compared to 1.176 Å in the gas phase. Thus, we would again classify this process as chemisorption. Although there is significant lengthening of the C-O bonds, complete dissociation to form CO+O is not observed due to the symmetric nature of the bond lengthening. Instead, a unidentate carbonate structure is formed upon surface adsorption, where the C-O distance between adsorbed CO$_2$ and the surface nO atom is 1.498 Å. On the catalyst, the Ce-O distances at the vacancy are significantly longer (2.292-2.237 Å) upon adsorption than the corresponding Ce-O distance in the clean reduced surface (2.165 Å). An additional depiction of this adsorption configuration (Rp5) is shown in Figure 6.5.

The next strongest energy of adsorption ($E_{ads} = -1.012$ eV) is observed for CO$_2$ parallel adsorption on top of the vacancy (Rp4). The two C-O bonds in the adsorbed CO$_2$ molecule are 1.198 Å and 1.311 Å, respectively. The adsorbed CO$_2$ molecule exhibits a similar binding geometry and bent configuration with Rp5; however, the O-C-O angle is slightly larger (140.4°) than the corresponding O-C-O angle in Rp5 (136.9°). Furthermore, the C-O distance between adsorbed CO$_2$ and the vacancy nO atom in Rp4 is also larger (1.642 Å), than the corresponding C-O distance in Rp5, which suggests that the adsorbed CO$_2$ molecule is not as activated as in the Rp5 configuration. Other parallel adsorption configurations are much less energetically stable, thus, we will not explore these configurations further.

Vertical adsorption atop the vacancy site (Rv1) is slightly less energetically favorable ($E_{ads} = -0.815$ eV) than for Rp5 or Rp4, and we observe no analogous activation of the CO$_2$ molecule; the resulting O-C-O angle is 177.1° and no significant changes are measured in the C-O bond lengths compared to the gas phase values. Though one oxygen atom of the CO$_2$ molecule is close to the split vacancy, the geometry of this site is just small enough to prevent an oxygen atom of CO$_2$ from inserting into the narrow split vacancy; thus, the CO$_2$ molecule in the Rv1 configuration cannot fully "heal" the vacancy to initiate the regeneration of the stoichiometric surface. Vertical adsorption atop the nCe atom nearest the vacancy site (Rv2), although similar to Rv(InP) for the in-plane vacancy, is less energetically favorable ($E_{ads} = -0.265$ eV) than adsorption atop the vacancy site (Rv1), even though the adsorbed molecule is bent similarly to Rp5. The other adsorption configurations on reduced ceria (110), where CO$_2$ is adsorbed far from the vacancy site, are even less energetically stable,
with energies of adsorption on the same order of magnitude as those on stoichiometric ceria (110); thus, we will not explore these configurations further.

In our comparison of the Rp5, Rv1, and Rv(InP) CO2 adsorption configurations, we note that Rp5 is the most energetically stable of the three. When we compared the energetic stability of the in-plane vs. split vacancy ceria (110) surfaces, we noted that the surface with a split vacancy was more stable, by 0.311 eV, than the surface with an in-plane vacancy. Now, CO2 adsorption on the split vacancy is still more stable, by 0.18 eV, than adsorption on the in-plane vacancy. Rp5 contains symmetrically elongated C-O bonds that favor carbonate formation, while Rv(InP) contains asymmetrically elongated C-O bonds that may promote dissociation to form carbon monoxide. Furthermore, vertical adsorption is favored only at the in-plane vacancy, while parallel adsorption is favored at the split vacancy. These differences in CO2 adsorption configuration as a function of the surface structure may contribute to the differences in the preferred mechanism and energetics of CO2 reduction.

6.3.3 Electronic Analysis of Ceria as a Catalyst for CO2 Activation

We seek to understand the underlying electronic structure effects that are responsible for the strong chemisorption of CO2 to reduced ceria (110) with a split oxygen vacancy. We believe that it is likely that the structural changes in the catalyst surface observed upon CO2 adsorption may be attributable to charge transfer between the surface and adsorbate molecule. We now analyze the electronic structure of the split vacancy system, and compare to the previously published electronic analysis of the in-plane vacancy structure [185, 159].

The partial electronic density of states (PEDOS) for Ce and O, when we have the clean (i.e., no adsorbate) reduced ceria (110) surface, is shown in Figure 6.7a, and it is consistent with those previously published in the literature [157, 158, 186]. We aligned the top of the valence band to 0 eV, and observed a filled gap state in the middle of the band gap; this filled gap corresponds to the unoccupied Ce 4f state. The integration of this peak indicates that there are two electrons per oxygen vacancy. To locate these two electrons, we plotted the excess electron spin density, which is defined as the difference between the up spin density and the down spin density, for clean reduced ceria (110), as shown in Figure 6.8a. We see that the spin density on the clean reduced ceria (110) surface is localized on the two nCe
atoms on the surface nearest the vacancy. The shapes of the two isosurfaces resemble those of $f$ orbitals, which is consistent with the $4f$ electronic configuration in Ce$^{3+}$. Since cerium exists in the Ce$^{4+}$ state in stoichiometric ceria, the excess electron spin density plot suggests that it adopts the Ce$^{3+}$ state upon formation of the oxygen vacancy. This result is also in agreement with previous observations on other reduced ceria surfaces [210].

![Figure 6.7](image_url)  
Figure 6.7: Partial electronic density of states (PEDOS) for Ce and O in reduced ceria (110). The top of the valence band is aligned to 0 eV, and the Fermi level is indicated with a vertical dashed line.

The PEDOS for Ce and O in the situation where CO$_2$ is adsorbed to reduced ceria (110) is shown in Figure 6.7b. We observe that the gap between the Fermi level (top of the unoccupied Ce $4f$ peak) and the bottom of the conduction band widens upon CO$_2$ adsorption, and nears the value observed for stoichiometric ceria (110) [150]. In addition, the filled gap state peak narrows upon CO$_2$ adsorption; the integration of this peak indicates that there is only one electron per oxygen vacancy, compared to two electrons in the clean reduced surface. To locate the remaining electron, we plotted the excess electron spin density for reduced ceria (110) with adsorbed CO$_2$ (Rp5), as shown in Figure 6.8b. From Figure 6.8b, we observe that the remaining electron is localized on the nCe$_2$ atom; thus one reduced Ce$^{3+}$ cation (nCe$_2$) remains on the surface, while the other (nCe$_1$) has been re-oxidized back to Ce$^{4+}$. The asymmetric electric field at the surface vacancy, with one Ce$^{3+}$ and one Ce$^{4+}$, explains the asymmetric C-O bond elongation found in the most stable adsorption configuration (Rp5). We also observe that the re-oxidized Ce$^{4+}$ atom is closer in distance to the nO oxygen atom that moved towards the vacancy site upon surface reduction, while the Ce$^{3+}$ atom is further

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from this NO oxygen atom and the adsorbed CO₂ molecule due to electrostatic repulsion. These results indicate that the reduced ceria (110) surface has been partially oxidized upon CO₂ adsorption at the vacancy site.

Since the CO₂ molecule may accept electrons into its lowest unoccupied molecular orbital to form the carbonate anion, we performed a Bader charge analysis on the system, focusing on the interface between CO₂ and the reduced ceria (110) surface, and plotted the electron localization function (ELF) [211]. From the variation of the Bader charges on the CO₂ molecule in various adsorption configurations (Table 6.1-Table 6.2), we observe definitive charge transfer from the ceria surface to the adsorbed CO₂ molecule. This is especially prominent in the case of the Rp5 configuration shown in Figure 6.8, where a net charge of $-0.955 |e|$ is transferred to form an adsorbed unidentate carbonate species that is especially stable ($E_{des} = +3.89$ eV). This is confirmed by the ELF plot shown in Figure 6.8c, where it can be seen that the adsorbed CO₂ is activated, with a net negative charge localized on the oxygen atoms of the molecule. When comparing to the most stable CO₂ adsorption at the in-plane vacancy (Rv(InP)), a net charge of $-0.923 |e|$ is transferred from the surface to the adsorbate molecule. Thus, ceria (110) containing either an in-plane or split oxygen vacancy may activate CO₂ via charge transfer to the molecule.

In summary, we conclude that the specific structure of the ceria surface has a critical influence on the CO₂ activation. CO₂ may chemisorb to reduced ceria (110) with an energy of adsorption of $-1.223$ eV, with charge transfer from the reduced ceria surface to the adsorbate resulting in the formation of an activated unidentate carbonate species. The reduced ceria (110) surface is only partially re-oxidized, which suggests that there is additional capacity for further reaction if the CO₂ concentration at the surface is increased. Our present findings, though conducted on the ceria (110) surface, are in agreement with related experimental work on the ceria (111) surface, in which the researchers showed that re-oxidation of the ceria surfaces using CO₂ would only be energetically feasible at the adsorption sites that have been sufficiently reduced [202]. Furthermore, partial re-oxidation of reduced ceria occurs with high reaction probability even at room temperature [202], so we propose that reduced ceria is a promising catalyst for CO₂ activation and further reaction.
6.3.4 CO$_2$ Dissociation on Reduced Ceria (110)

The results presented above show that CO$_2$ adsorbs strongly on reduced ceria (110) surfaces, with the split oxygen vacancy being preferred slightly over the in-plane vacancy. We infer that the adsorption process itself results in a significant weakening of the C-O bonds of the carbon dioxide molecule. Thus, we seek to determine how these differences in structure and electronic properties, for both the catalyst and adsorbate, may dictate the reactivity of the system with respect to CO$_2$ dissociation to form CO, which we choose among several possibilities for CO$_2$ for its conceptual similarity to the reverse process of CO oxidation. With the dissociation of a C-O bond, the resulting O atom may "heal" the surface vacancy to regenerate the stoichiometric ceria surface. We now show the proposed reaction pathways, including transition states and intermediates, for this process at the in-plane and split oxygen vacancies.

The proposed carbon cycle is shown in Figure 6.9, based on the different most stable adsorption configurations for CO$_2$ and its dissociation products on the in-plane and split vacancy structures. The local minima and saddle points on the multi-dimensional potential energy surface were identified and optimized from the NEB method. The computed energies of activation are also shown.

On the in-plane vacancy structure, we see that CO$_2$ dissociation proceeds from the Rv(InP) inorganic bidentate carboxylate (pathway a). On the split vacancy structure, we see that the CO$_2$ dissociation proceeds from the Rp5 unidentate carbonate (pathway b). All energies are normalized by setting the total energy of the final state of both pathways, namely the p (2 × 2) supercell of the stoichiometric ceria (110) surface with adsorbed CO, to be 0 eV.

The dissociation process initiated from the Rv(InP) adsorption configuration is depicted in Figure 6.10a. The reaction involves an initial interconversion from the inorganic bidentate carboxylate species to an unsymmetric bridged carbonate species (stage 2a), with an activation energy barrier of +1.613 eV. In this step, the C atom moves toward the saturated surface O atom neighboring the in-plane vacancy, and pulls it out the surface to form a new C-nO bond by breaking the O-nnCe bond. In the second step of the pathway, the asymmetric bridged carbonate reconstructs into a symmetric bridged (bidentate) carbonate (stage 3a) to mitigate the steric effect, and must overcome only a small energy barrier of +0.172
eV. For the symmetric bridged carbonate structure, the lengths of the C-O$_{g2}$ bond and C-O$_{v}$ bond are 1.362 Å and 1.368 Å, respectively, while the length of the upward C-O$_{g1}$ bond is 1.244 Å; thus, the system appears to be ripe for CO formation. The calculated energy of desorption is +1.891 eV, which indicates that CO is strongly adsorbed on this surface. In fact, the bridged carbonate configuration (stage 3a) shown in Figure 6.10a has been identified previously by other researchers as the result of CO adsorption to the stoichiometric ceria (110) surface [191, 206]. The reported energy of adsorption is -1.95 eV [206], which is slightly larger than the value of -1.89 eV determined in this study. The overall energy required for CO$_2$ dissociation at an in-plane vacancy is +1.065 eV, which is quantitatively consistent with the reported results for CO oxidation on stoichiometric ceria (110) [212, 213, 214, 209].

The dissociation process initiated from the Rp5 adsorption configuration is depicted in Figure 6.10b. The first step involves the O$_{g2}$ atom of the bent CO$_2$ molecule moving toward the surface and binding to the surface Ce site with excess electron spin density (stage 1b); we note that the other surface Ce site has already been re-oxidized during the CO$_2$ adsorption step. For stage 2b, we observe the apparent shortening of the C-O$_{g1}$ bond and the lengthening of the C-O$_{g2}$ bond, due to additional charge transfer from the surface; this, we believe, represents a transition state in the formation of carbon monoxide (C=O$_{g1}$). Also we note that two of the three oxygen atoms in the unidentate carbonate anion now bind to the same Ce atom, so we have formed an asymmetric bidentate carbonate structure. This step overcomes an energy barrier of +1.286 eV. In the second step, the C-O$_{g2}$ bond is further elongated before finally breaking to form an adsorbed CO molecule, with the remaining O$_{g2}$ left on the surface to heal the split vacancy. Since the Ce cation is more electrophilic than the saturated O anion, the CO molecule then diffuses from the (former) oxygen vacancy site to the surface Ce site. The calculated energy of desorption is -0.263 eV, which is comparable to the previously reported energy of desorption of -0.2 eV for CO on the stoichiometric ceria (110) surface [191]. The overall energy required for CO$_2$ dissociation at a split vacancy is +1.359 eV.

While CO$_2$ dissociation at the split vacancy is less energetically favorable than the equivalent process at the in-plane vacancy, the path-independent overall energy of reaction is preserved when we consider that the formation of the split vacancy is more energetically favorable than the formation of the in-plane vacancy. We also note that the highest energy of activation for CO$_2$ dissociation at the in-plane vacancy is +1.613 eV to form TS1, while the highest energy
of activation for CO$_2$ dissociation at the split vacancy is +1.359 eV to form TS2; thus, the rate-limiting steps for the respective dissociation pathways may differ and it appears that CO$_2$ dissociation may be favored kinetically at the split vacancy even though it may be favored thermodynamically at the in-plane vacancy. However, when considering the process in reverse, the bridged carbonate (stage 3a) is very energetically stable, so CO oxidation may follow the in-plane vacancy pathway. Since all of the energies of activation appear to be quite high (i.e., +1.3 eV at a minimum, which is higher than $E_{des}$ for CO$_2$), it appears that one must add charge carriers, such as additional oxygen vacancies or even protons, to the catalyst surface to lower the energies of activation and achieve more efficient CO$_2$ conversion at favorable operating conditions. This will be investigated in the next chapter.

6.4 Conclusions

We have performed analyses of structural geometries, electronic properties, and reaction energetics for carbon dioxide activation and dissociation on ceria (110) surfaces, using density functional theory with the Hubbard $U$ correction. We find that the structure of the oxygen vacancy at the reduced surface plays an important role in the activation of CO$_2$ on the ceria surface, and that the formation of the split vacancy is energetically favored over the in-plane vacancy by 0.311 eV. CO$_2$ adsorption to reduced ceria (110) is energetically favored, particularly in the case of parallel CO$_2$ adsorption atop the split oxygen vacancy, which has an energy of adsorption of -1.223 eV. This chemisorption process results in a bent CO$_2$ molecule with an O-C-O angle of 136.9° and elongated C-O bonds compared to the gas-phase molecule. The Bader charge analysis confirms that a net charge of $-0.955 |e|$ is transferred from the reduced ceria (110) surface to the adsorbed CO$_2$ molecule at the split vacancy, and a net charge of $-0.923 |e|$ is transferred to the adsorbed CO$_2$ molecule at the in-plane vacancy. Thus, the CO$_2$ molecule is activated at oxygen vacancies, following which the reduced ceria (110) surface is partially re-oxidized. When analyzing the elementary steps comprising CO$_2$ dissociation at both types of oxygen vacancies, we find that: 1. On the in-plane vacancy, CO$_2$ proceeds to first form an inorganic bidentate carboxylate, then a symmetric bridged carbonate, and finally CO, and 2. On the split vacancy, CO$_2$ proceeds to first form a unidentate carbonate, then an asymmetric bidentate carbonate, and finally CO. The in-plane pathway has, for its purported rate-limiting step, an energy of activation
of +1.613 eV and an overall reaction energy of +1.065 eV, while the split pathway has, for its purported rate-limiting step, an energy of activation of +1.359 eV and an overall reaction energy of +1.375 eV. These subtle differences in the energies of activation for the elementary steps suggest that CO$_2$ dissociation is favored on the split vacancy, while the reverse process of CO oxidation may favor the formation of the in-plane vacancy. Reduced ceria (110) represents a promising catalyst for either thermal or electrochemical reduction of CO$_2$ as the first step in the formation of fuels and chemicals as a means of closing of the carbon cycle.
Figure 6.8: Excess electron spin density (ESD) and electron localization function (ELF) for reduced ceria (110) with adsorbed CO$_2$ (Rp5). Upon formation of the oxygen vacancy, adjacent cerium atoms are reduced to Ce$^{3+}$. Upon CO$_2$ adsorption, one cerium cation is re-oxidized back to Ce$^{4+}$ and the excess charge of $-0.955|e|$ is transferred to the adsorbate. An adsorbed unidentate carbonate species is formed. The Ce-O bonds at the surface are also lengthened.
Figure 6.9: Proposed carbon cycle for interconversion between CO$_2$ and CO, with reduced ceria (110) possessing either an in-plane vacancy or a split vacancy.
Figure 6.10: CO$_2$ dissociation pathways on reduced ceria (110) with in-plane or split oxygen vacancy.
Chapter 7

CO₂ Hydrogenation to Methanol

We note that the highest energy of activation for CO₂ dissociation on the reduced ceria surface with the in-plane vacancy is +1.613 eV, while the highest energy of activation for CO₂ dissociation on the reduced ceria surface with the split vacancy is +1.359 eV; thus, the rate-limiting steps for the respective dissociation pathways may differ and it appears that CO₂ dissociation may be favored kinetically at the split vacancy even though it may be favored thermodynamically at the in-plane vacancy. However, since all of the energies of activation appear to be quite high, it appears that one must add charge carriers, such as protons, to the catalyst surface to lower the energies of activation and achieve more efficient CO₂ conversion at favorable operating conditions. The protons can be obtained from methane dehydrogenation as we discussed in chapter 3 and 4. Methanol can be synthesized by adding protons to the CO₂ molecule. This reaction is known as CO₂ hydrogenation.

In fact, the hydrogenation of CO₂ to methanol is receiving more and more attention because of both the industrial importance in fuel production and the environmental significance in greenhouse gas utilization [215]. Methanol is an efficient energy form suitable for storage and transportation. More importantly, methanol can be used as the raw material for other synthetic hydrocarbons by the MTO (methanol to olefin) process. The CO₂ generated from the use of CH₃OH as a liquid fuel can be chemically recycled by converting it to CH₃OH through hydrogenation [216].

Although industrial methanol synthesis technology has been developed for almost 100 years, several key mechanistic questions have not been answered. CO once was assumed to be
the main reactant from CO$_2$ reduction for methanol synthesis until the isotope labeling experiments by Chinchen et al. strongly suggested that CO$_2$ is the main carbon source [217]. A recent paper by Grabow and Mavrikakis contains a thorough review of the current state of our understanding in CO$_2$ hydrogenation and indicates that the details of the mechanism are more complex than previously thought and depends on the catalyst active sites [218].

Previously found the oxygen vacancy on reduced ceria catalyst can effectively activate CO$_2$. The chemisorption process results in a bent CO$_2$ molecule with an O-C-O angle of 136.9° and elongated C-O bonds compared to the gas-phase molecule. The reduced ceria (110) surface is partially re-oxidized correspondingly [153].

We now implement the first statistical kinetics model to describe the hydrogenation of CO$_2$ on the reduced ceria surface. The kinetic model relies on first principles density functional theory calculations, which were previously utilized to model the surface structure, investigate thermodynamic properties and explore the reaction mechanism.

We show here that multiple reaction paths are present for CO$_2$ hydrogenation into methanol on the reduced ceria (110) surface. The DFT calculations were carried out to search for the stable states and favorable energy pathways. The contribution of each reaction path to methanol formation was thus assessed explicitly in terms of reaction rate.

### 7.1 Hydrogenation Network and mechanism

We previously showed that CO$_2$ adsorption on both reduced ceria (110) surfaces is thermodynamically favored over the corresponding adsorption on stoichiometric ceria (110), but the most stable adsorption configuration consists of CO$_2$ adsorbed parallel to the reduced ceria (110) surface at a split vacancy. In contrast to CO$_2$ adsorption at the split vacancy, we found that H atoms only adsorb strongly on the surface oxygen site with the adsorption energy of 2.64 eV, thus we can know H atoms will prefer to adsorb on O and cannot diffuse to Ce site (7.1). Kinetically, H$_2$ dissociation on ceria surface requires a reaction barrier of 1.48 eV, which is much higher than the barrier of CH$_4$ dehydrogenation on Pt nanoclusters.
(Chapter 3 and 4); this is consistent with our assumption that CO$_2$ hydrogenation on ceria may occur with the protons generated from CH$_4$ dehydrogenation on Pt nanoclusters. Due to computational limitations, the Pt cluster is not included in the subsequent calculations, although we acknowledge that the true activity of the active sites may vary somewhat from the those calculated here on reduced ceria.

![Diagram of ceria surface with CO$_2$ and H adsorption](image)

Figure 7.1: top view and side view for clear reduced ceria surface and reduced ceria surface with H and CO$_2$

We now examine the reactions for CO$_2$ hydrogenation by starting from CO$_2$ adsorbed at split vacancy site, with H binding either to C atom to form HCOO$^*$ or to O atom to form COOH$^*$. We know that at present, it is almost impossible to provide an exhaustive first-principles account of the kinetics of the complex system of CO$_2$ hydrogenation. However, in
determining the reaction network, we still consider all possible intermediates with extensive modeling. We take a three-step approach: (i) all likely H binding sites for a new given intermediate are first examined; (ii) guided by the estimation of intermediate stability and calculation of reaction barriers, we only keep the most stable intermediates and continue along the low barrier reaction channels to reach the next new intermediate and thus reject those intermediates with too high barriers that are too high (e.g., barriers larger than 1 eV); and (iii) we repeat (i)(ii) until methanol is produced. By this approach, the reaction network with all possible intermediates is obtained as shown in Figure 7.2.

For HCO*, H₂CO*, HCOO*, H₂COO*, H₃CO* and H₂COOH* intermediates, they all adsorb at the vacancy site with their O ends. DFT calculations show that their adsorption energies at this initial site are generally much higher than the corresponding values on a neighboring ceria atom site by more than about 0.45 eV, which indicates that the diffusion of these O-containing species over to ceria sites is unlikely.

The simplified network after stability screening is obtained as shown in Figure 7.3. The barrier analysis ultimately identifies two routes leading to methanol, namely the HCOO route and the COOH route, as shown in Figure 7.4.

![Figure 7.2: Hydrogenation network](image)
Figure 7.3: Hydrogenation network after stability screening

Figure 7.4: Hydrogenation mechanism
From Figure 7.4, we find there are seven gas phase species involved in CO$_2$ hydrogenation reactions: CO$_2$, H$_2$, CO, HCOOH, CH$_2$O, CH$_3$OH, H$_2$O. As the main product and important side products, the CH$_3$OH, HCOOH and CH$_2$O structures are shown in Figure 7.5

![HCOOH(ad) $E_{ad} = -0.12$ eV](image)

![CH$_2$O (ad) $E_{ad} = -0.63$ eV](image)

![CH$_3$OH (ad) $E_{ad} = -0.29$ eV](image)

Figure 7.5: Stable adsorption configuration of HCOOH, CH$_2$O, CH$_3$OH on ceria vacancy

We further calculate the energy barrier of each elementary step in the two pathways to methanol for detailed understanding of mechanism. The energy profiles are shown in Figure 7.6.

The HCOO route (Formate route) initiates by the direct hydrogenation of CO$_2$ to yield HCOO$^*$. At the first transition state (TS), the formed C-H bond distance is 1.62 Å and the calculated barrier height $E_a$ is 0.26 eV. The low barrier is also noted in the first hydrogenation step of the COOH route (carbonate route) with an energy barrier of 0.35 eV. Next, one more H can be sequentially added to form H$_2$COO$^*$. The internal C-O bond is weakened by the addition of H and it can break at the stage of H$_2$COOH$^*$, leading to the formation of H$_2$CO$^*$ and OH$^*$. H$_2$CO$^*$ can further be hydrogenated to H$_3$CO$^*$ and finally H$_3$COH$^*$. It should be mentioned that a H$_2$CO$^*$ gas molecule can be obtained in this process, but it adsorbs strongly at the surface vacancy with a relatively strong O-Ce bonding and 0.64 eV adsorption energy. Considering that its hydrogenation barrier is 0.49 eV, H$_2$CO$^*$ formed at the surface would prefer to undergo hydrogenation rather than desorption or diffusion to Ce sites. This process is exothermic (0.2 eV). It implies that once CO$_2$ is captured via hydrogenation to form H$_3$CO$^*$, the reverse reaction is unlikely to occur. It is worth mentioning that the cleavage of the C-O bond of H$_3$CO to yield CH$_3$ and O is very difficult, with a barrier of 1.78 eV, which is much higher than the direct hydrogenation of H$_3$CO$^*$. This means that
the production of the byproduct methane (CH$_4$) is kinetically inhibited. This indicates that CO$_2$ hydrogenation hardly has any selectivity to CH$_4$ over a reduced ceria catalyst.

### 7.2 Thermodynamic Properties of CO$_2$ Hydrogenation

#### 7.2.1 Thermodynamic model and validation on gas-phase species

Next, we investigate the thermodynamic properties of CO$_2$ hydrogenation. A vibrational analysis was carried out in order to validate the optimized geometry of the adsorbed species and to determine vibrational frequencies of transition states. All atoms of ceria were rigidly constrained during these calculations. The Hessian dynamical matrix is obtained by numerical differentiation of the forces and diagonalized, which yields the harmonic molecular frequencies and the normal modes. These calculations make it possible to compute zero-point energy (ZPE) corrected energies and partition functions [219].
For gas phase species, the translational, rotational, and vibrational entropies are well defined, in particular the vibrational entropy, $S_{\text{vib}}$, can be directly obtained from the vibrational partition function, using the DFT-estimated frequencies, $v_i$:

$$S_{\text{vib}}(T) = \sum_{n=1}^{N} \left[ \frac{h v_i}{T} \frac{X_i}{1 - X_i} - k_B \ln(1 - X_i) \right]$$ (7.1)

where $X_i = e^{-h v_i / k_B T}$

The heat capacity, $C_p = T \left( \frac{\partial S}{\partial T} \right)_p$, can then be computed numerically by differentiating the entropy. The calculated gas phase entropy and heat capacity of formic acid, formaldehyde and methanol are shown in Figure 7.7 and 7.8. Also, the tabulated values from Yaw’s handbook as computed from the Shomate equation for entropy and a polynomial for heat capacity for these species, are given for comparison. From Figure 7.7 and 7.8, we can see the relative errors for entropy are less than 10%, while the relative errors for heat capacity are less than 15%. Thus, based on DFT-estimated vibrational frequencies, we can obtain good agreement with experimental values for the gas phase species.

To obtain enthalpy, $H$, estimates at finite temperature, $T$, for all adsorbed species and products, we correct the electronic energy for the zero point energy (ZPE) contribution and temperature variation using $C_p$. The equation is shown as below:

$$H(T) = H(0 \text{ K}) + \int_0^T C_p(T') dT'$$ (7.2)

Numerically, $T = 0$ K results in an undefined value during the evaluation of $C_p$, as the temperature appears in the denominator. We can approximate $H(0 \text{ K}) \approx H(1 \text{ K})$, and obtain its value by $H(1 \text{ K}) = U(0 \text{ K}) + ZPE$, where $U$ is the total energy. Thus, we can obtain the reaction enthalpy, $\Delta H_{\text{rxn}}$ for every elementary reaction at finite temperatures.
Figure 7.7: Comparison of calculated DFT entropies with tabulated entropies in Yaw’s handbook for gas phase formic acid (black), formaldehyde (blue) and methanol (red).

Figure 7.8: Comparison of calculated DFT heat capacities with tabulated heat capacities in Yaw’s handbook for gas phase formic acid (black), formaldehyde (blue) and methanol (red).
7.2.2 Extension to surface-adsorbed species

Within the framework of our thermodynamics model, we now develop a related equation to calculate the reaction enthalpy from first principles, with calculations of dissociation energy, adsorption energy and desorption energy that are included in a free thermodynamic cycle (Figure 7.9).

\[
\Delta H_{\text{rxn}}(T) = \Delta H_{\text{rxn,DFT}}(T) + \sum_{n=1}^{N} E_{\text{ad}} + E_{\text{diss}} + \sum_{m=1}^{M} E_{\text{de}} \tag{7.3}
\]

where \( E_{\text{ad}} \) and \( E_{\text{de}} \) correspond to the adsorption and desorption energy, respectively, which are obtained from DFT calculations for the most stable adsorption configurations. The reaction enthalpy at finite temperature, \( \Delta H_{\text{rxn,DFT}}(T) \), is calculated from the individual enthalpies of the reactants and products on our ceria catalyst. \( \Delta H_{\text{rxn}} \) is the difference between the energies of the final state and initial state at a given temperature. Similarly \( \Delta S_{\text{rxn}} \) can be calculated.

The main reaction and side reactions are shown below:

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \tag{7.4}
\]
\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (7.5)
\]

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH} \quad (7.6)
\]

\[
\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \quad (7.7)
\]

\[
\text{CO}_2 + 2\text{H}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \quad (7.8)
\]

\[
\text{CH}_2\text{O} + \text{H}_2 \rightarrow \text{CH}_3\text{OH} \quad (7.9)
\]

We calculate changes of entropy and reaction enthalpies of all of these reactions in both the gas and adsorbed phases, and show the results in Table 7.1. We again compare our results to the only available experimental values in the NIST database, which are for the corresponding gas-phase reactions. The differences in the calculated entropies of reaction show absolute errors of less than 15 J/mol/K (relative errors less than 10 %)

Table 7.1: Entropy changes \(\Delta S_{rxn}\) for main reactions related to CO\(_2\) hydrogenation at 298 K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta S_{rxn}) (298 K) J/mol/K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT gas phase</td>
</tr>
<tr>
<td>(\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O})</td>
<td>-191.95</td>
</tr>
<tr>
<td>(\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O})</td>
<td>38.23</td>
</tr>
<tr>
<td>(\text{CO} + 2\text{H}_2 \rightarrow \text{HCOOH})</td>
<td>-102.98</td>
</tr>
<tr>
<td>(\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH})</td>
<td>-229.23</td>
</tr>
<tr>
<td>(\text{CO}_2 + 2\text{H}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O})</td>
<td>-78.91</td>
</tr>
<tr>
<td>(\text{CH}_2\text{O} + \text{H}_2 \rightarrow \text{CH}_3\text{OH})</td>
<td>-157.93</td>
</tr>
</tbody>
</table>

The main error in the DFT-calculated entropies of reaction can be almost entirely attributed to the enthalpy of \(\text{H}_2\text{O}\) desorption from the surface. When \(\text{H}_2\text{O}\) is destabilized by 0.3 eV
Table 7.2: Enthalpy changes $\Delta H_{rxn}$ for main reactions related to CO$_2$ hydrogenation at 298 K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_{rxn}$ (298 K) kJ/mol</th>
<th>DFT gas phase</th>
<th>DFT on catalyst</th>
<th>DFT corrected</th>
<th>NIST database</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + 3H$_2$ → CH$_3$OH + H$_2$O</td>
<td>-102.31</td>
<td>-102.31</td>
<td>-87.91</td>
<td>-58.96</td>
<td>-53.31</td>
</tr>
<tr>
<td>CO$_2$ + H$_2$ → CO + H$_2$O</td>
<td>-12.73</td>
<td>6.62</td>
<td>35.57</td>
<td>41.17</td>
<td></td>
</tr>
<tr>
<td>CO$_2$ + H$_2$ → HCOOH</td>
<td>39.45</td>
<td>23.85</td>
<td>23.85</td>
<td>14.92</td>
<td></td>
</tr>
<tr>
<td>CO + 2H$_2$ → CH$_3$OH</td>
<td>-129.78</td>
<td>-105.29</td>
<td>-105.29</td>
<td>-94.47</td>
<td></td>
</tr>
<tr>
<td>CO$_2$ + 2H$_2$ → CH$_3$O + H$_2$O</td>
<td>-8.06</td>
<td>14.13</td>
<td>43.08</td>
<td>35.81</td>
<td></td>
</tr>
<tr>
<td>CH$_2$O + H$_2$ → CH$_3$OH</td>
<td>-138.45</td>
<td>-97.23</td>
<td>-97.23</td>
<td>-89.12</td>
<td></td>
</tr>
</tbody>
</table>

(28.95 kJ/mol) on the surface, it can result in $\Delta H_{DFT,corrected}$ values that are in better agreement with the values from the NIST database.

We applied this method to calculate surface phase reaction enthalpies at higher temperatures. The reference values were obtained from the Shomate equation. The results are shown in Table 7.3

Table 7.3: Enthalpy changes $\Delta H_{rxn}$ for main surface-phase reactions related to CO$_2$ hydrogenation at finite temperatures (400 K-1000 K).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H_{rxn}$ kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400K</td>
</tr>
<tr>
<td>CO$_2$ + 3H$_2$ → CH$_3$OH + H$_2$O</td>
<td>-47.27</td>
</tr>
<tr>
<td>CO$_2$ + H$_2$ → CO + H$_2$O</td>
<td>43.59</td>
</tr>
<tr>
<td>CO$_2$ + H$_2$ → HCOOH</td>
<td>15.10</td>
</tr>
<tr>
<td>CO + 2H$_2$ → CH$_3$OH</td>
<td>-90.87</td>
</tr>
<tr>
<td>CO$_2$ + 2H$_2$ → CH$_3$O + H$_2$O</td>
<td>39.04</td>
</tr>
<tr>
<td>CH$_2$O + H$_2$ → CH$_3$OH</td>
<td>-86.31</td>
</tr>
</tbody>
</table>

For these reactions where H$_2$O is not involved, the enthalpy changes show absolute errors of less than 15 kJ/mol when the reaction temperature is between 298 K-800 K. For reactions where H$_2$O involved, enthalpy changes show absolute errors of less than 15 kJ/mol when the reaction temperature is 400 K-800 K. However, the deviation is large when the temperature
Figure 7.10: Deviation between $\Delta H_{\text{rxn}}$ and $\Delta H_{\text{DFT,corrected}}$ for reaction not involving $\text{H}_2\text{O}$ is below 400 K; this may be because $\text{H}_2\text{O}$ has a higher boiling point than other species in this reaction network. These results show the thermodynamics of $\text{CO}_2$ hydrogenation, and provide evidences that our temperature-dependent model can accurately predict the reaction enthalpy at normal operating temperatures. It is quantitatively accurate for calculations on small hydrocarbon compounds reacting at 298 K-800 K (no water), and at 400 K-800 K (with water), with relative errors of less than 10%. Therefore, this method is generally applicable to the thermodynamics of surface-phase reactions.

### 7.3 Rate constants for $\text{CO}_2$ hydrogenation

Within the framework of a microkinetic model, the experimental activation energy cannot be fitted independently, due to the thermodynamic constraint that $\Delta H_{\text{rxn}}$ equals the difference between the forward activation energy barrier, $E_{a,f}$, and reverse activation energy barrier,
E_{a,r}$. Hence, we develop a related equation to calculate the activation energy for elementary reaction:

$$E_{a,f} (T) = E_{a,f,DFT} + \beta (\Delta H_{rxn} (T) - \Delta E_{rxn,DFT})$$  \hspace{1cm} (7.10)$$

where $E_{a,f,DFT}$ corresponds to the forward activation energy barrier at 0 K, which is obtained from DFT calculations. The reverse activation energy barrier from DFT can be obtained from Figure 7.6. The reaction enthalpy at finite temperature, $\Delta H_{rxn} (T)$, is calculated from the individual enthalpies of the initial state and the final state for the constituent elementary reactions, since we have already shown that it is quantitatively comparable to the experimental value. $\Delta E_{rxn,DFT}$ is the difference between the energies of final state and initial state at 0 K. The variable $\beta$ denotes the relative position of the transition state compared to the initial (i.e., $\beta = 0$) or final (i.e., $\beta = 1$) state of the relevant elementary reaction. It can be obtained by considering which image in the CI-NEB calculations (out of four) corresponds to the transition state. When the value of $\beta$ is close to 0, it describes
to an initial-like transition state; thus, the forward activation energy may be kept at the DFT value, while the reverse activation energy is temperature dependent and needs to be thermodynamically calculated by analogy to Equation 7.10. When the value of $\beta$ is close to 1, it corresponds a final-like transition state; thus, the reverse activation energy may be kept at the DFT value, while the forward activation energy is corrected using Equation 7.10. Otherwise, for intermediate values of $\beta$, the difference between $\Delta H_{\text{rxn}}(T) - \Delta E_{\text{rxn,DFT}}$ affects both the forward activation energy and reverse activation energy. This calculation technique is based on the Brønsted-Evans-Polanyi relationship, which states that the difference in activation energy between two reactions of the same family is proportional to the difference of their enthalpies of reaction [220, 221, 222].

The energies of activation at the transition states are also corrected in a similar manner using ZPE and $C_p$. The pre-exponential factor, $A$, is calculated from the entropy differences between the initial and transition states of the respective elementary step as below,

$$A(T) = \left(\frac{k_B T}{h}\right) \left(\frac{Q_{TS}}{Q_0}\right)$$  \hspace{1cm} (7.11)

where $Q_{TS}$ and $Q_0$ are the vibrational partition functions of transition states and initial states, respectively. $k_B$ is Boltzmann's constant, and $h$ is Planck's constant.

The mathematical and thermodynamical expressions above enable us to obtain the relationship between reaction rate coefficients and temperature by the Arrhenius equation, using the calculated $E_{a,f}(T)$ and $A(T)$.

$$k(T) = A(T) \exp \left( -\frac{E_{a,f}(T)}{k_B T} \right)$$ \hspace{1cm} (7.12)

From this non-equilibrium thermodynamics approach, we can obtain the reaction enthalpy and the activation energy of every elementary step of CO$_2$ hydrogenation by the modification above. Industrially, CO$_2$ hydrogenation to CH$_3$OH is conducted at 493-573 K [223]. Therefore, we choose 500 K to provide a first estimate of the rate constants, as shown in Table 7.4.
Table 7.4: Rate constants for elementary steps of CO$_2$ hydrogenation on reduced ceria (110) at 500 K.

<table>
<thead>
<tr>
<th>no.</th>
<th>Elementary reaction ($T=500$ K, $P=1$ atm)</th>
<th>$k_{forward}$ (s$^{-1}$)</th>
<th>$k_{backward}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1$</td>
<td>$\text{CO}_2(g) + ^* \rightarrow \text{CO}_2^*$</td>
<td>1.95e+04</td>
<td>3.23e+01</td>
</tr>
<tr>
<td>$r_2$</td>
<td>$\text{CO}_2^* + \text{H}^* \rightarrow \text{COOH}^* + ^*$</td>
<td>2.67e+04</td>
<td>5.19e+04</td>
</tr>
<tr>
<td>$r_3$</td>
<td>$\text{COOH}^* + ^* \rightarrow \text{CO}^* + \text{OH}^*$</td>
<td>6.31e+03</td>
<td>3.13e+05</td>
</tr>
<tr>
<td>$r_4$</td>
<td>$\text{COOH}^* + \text{H}^* \rightarrow \text{HCOOH}^* + ^*$</td>
<td>3.11e+01</td>
<td>1.78e+02</td>
</tr>
<tr>
<td>$r_5$</td>
<td>$\text{HCOOH}^* \rightarrow \text{HCOOH}(g) + ^*$</td>
<td>2.17e+03</td>
<td>4.21e+03</td>
</tr>
<tr>
<td>$r_6$</td>
<td>$\text{CO}^* \rightarrow \text{CO}(g) + ^*$</td>
<td>1.02e+01</td>
<td>3.57e+03</td>
</tr>
<tr>
<td>$r_7$</td>
<td>$\text{CO}^* + \text{H}^* \rightarrow \text{HCO}^* + ^*$</td>
<td>4.24e+06</td>
<td>3.82e+06</td>
</tr>
<tr>
<td>$r_8$</td>
<td>$\text{HCO}^* + \text{H}^* \rightarrow \text{HCOOH}^* + ^*$</td>
<td>3.82e-03</td>
<td>1.31e-02</td>
</tr>
<tr>
<td>$r_9$</td>
<td>$\text{HCOOH}^* + \text{H}^* \rightarrow \text{H}_2\text{COOH}^* + ^*$</td>
<td>7.33e-03</td>
<td>5.41e-03</td>
</tr>
<tr>
<td>$r_{10}$</td>
<td>$\text{H}_2\text{COH}^* + \text{H}^* \rightarrow \text{H}_3\text{COH}^* + ^*$</td>
<td>6.55e-03</td>
<td>8.21e-04</td>
</tr>
<tr>
<td>$r_{11}$</td>
<td>$\text{CO}_2^* + \text{H}^* \rightarrow \text{HCOOH}^* + ^*$</td>
<td>3.91e+04</td>
<td>3.55e+02</td>
</tr>
<tr>
<td>$r_{12}$</td>
<td>$\text{HCOOH}^* + \text{H}^* \rightarrow \text{H}_2\text{COO}^* + ^*$</td>
<td>5.11e+03</td>
<td>8.26e+05</td>
</tr>
<tr>
<td>$r_{13}$</td>
<td>$\text{H}_2\text{COO}^* + \text{H}^* \rightarrow \text{H}_2\text{COOH}^* + ^*$</td>
<td>7.63e+03</td>
<td>5.19e+02</td>
</tr>
<tr>
<td>$r_{14}$</td>
<td>$\text{H}_2\text{COOH}^* + ^* \rightarrow \text{H}_2\text{CO}^* + \text{OH}^*$</td>
<td>4.55e-04</td>
<td>1.98e-02</td>
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<tr>
<td>$r_{15}$</td>
<td>$\text{H}_2\text{CO}^* \rightarrow \text{H}_2\text{CO}(g) + ^*$</td>
<td>1.02e+01</td>
<td>2.82e+03</td>
</tr>
<tr>
<td>$r_{16}$</td>
<td>$\text{H}_2\text{CO}^* + \text{H}^* \rightarrow \text{H}_3\text{CO}^* + ^*$</td>
<td>3.76e+01</td>
<td>5.43e+01</td>
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<tr>
<td>$r_{17}$</td>
<td>$\text{H}_3\text{CO}^* + \text{H}^* \rightarrow \text{H}_3\text{COH}^* + ^*$</td>
<td>9.21e+00</td>
<td>2.13e-01</td>
</tr>
<tr>
<td>$r_{18}$</td>
<td>$\text{H}_3\text{COH}^* \rightarrow \text{H}_3\text{COH}(g) + ^*$</td>
<td>8.33e+01</td>
<td>4.08e+02</td>
</tr>
<tr>
<td>$r_{19}$</td>
<td>$\text{H}^* + \text{OH}^* \rightarrow \text{H}_2\text{O}^* + ^*$</td>
<td>5.91e-03</td>
<td>3.41e-05</td>
</tr>
<tr>
<td>$r_{20}$</td>
<td>$\text{H}_2\text{O}^* \rightarrow \text{H}_2\text{O}(g) + ^*$</td>
<td>7.32e+02</td>
<td>2.45e+02</td>
</tr>
<tr>
<td>$r_{21}$</td>
<td>$\text{H}_3(g) + 2^* \rightarrow 2\text{H}^*$</td>
<td>5.89e+01</td>
<td>2.87e+01</td>
</tr>
</tbody>
</table>
By comparing all elementary reaction rate constants at 500 K, we found that the dissociation of $\text{H}_2\text{COH}^*$ to HCOH$^*$ and H$^*$ is the slowest step for the COOH route, while the hydrogenation of $\text{H}_2\text{COOH}^*$ is the slowest one for the HCOO route.

The dissociation of adsorbed COOH$^*$ to produce CO$^*$ and OH$^*$ is an endothermic process, and the reverse rate constant of $3.13 \times 10^5 \text{s}^{-1}$ is not only about two orders of magnitude larger than the forward one, but also four orders of magnitude larger than COOH$^*$ hydrogenation. Such a significant rate demonstrates that the consumption of the surface COOH$^*$ by hydrogenation is not sufficient enough to prevent the reverse direction of the dissociation reaction from occurring. In other words, the formed CO$^*$ and OH$^*$ would quickly react back to the original COOH$^*$ groups. Besides, we can see the formation and dissociation of $\text{H}_2\text{O}$ both are slow, though the formation rate constant is about two orders of magnitude larger than the reverse one. Thus, the formate (HCOO$^*$ ) route appears more likely to result in methanol production.

### 7.4 Conclusion

We studied the conversion of CO$_2$ to methanol by hydrogenation on reduced ceria (110). We gained mechanistic, thermodynamic, and kinetic insight into the elementary steps that comprise larger reaction networks of interest to the broader catalysis community. We used density functional theory calculations and a microkinetics technique to elucidate the nature of the small carbon-containing species formed during this reaction, and determined how catalyst structure dictates activity and selectivity. In all possible intermediates, our calculation results show that HOCOH$^*$, HCOOH$^*$ and COH$^*$ are not feasible due to the high formation energy. Also, direct formyl hydrogenation to formaldehyde (H$_2$CO), the key intermediate for methanol synthesis, is not feasible due to the high activation barrier. Instead, we find that H-formalin to formaldehyde is kinetically more favorable. The formaldehyde then converts into methoxy, $\text{H}_3\text{CO}^*$, rather than $\text{H}_2\text{COH}^*$, followed by a consecutive hydrogenation step to form methanol. Thus, two reaction channels to methanol are identified (i) COOH pathway via a carboxyl intermediate and (ii) HCOO pathway via a formate intermediate. The rate-limiting step of each pathway and the theoretical selectivity is determined.
We developed a non-equilibrium thermodynamics method to calculate energies of activation and rate constants of CO$_2$ hydrogenation at finite temperatures, based on DFT barriers and the modified Bronsted-Evans-Polanyi principle. Also, we applied a numerical approach to compute heat capacities and reaction enthalpy based on the vibrational frequency results from DFT and partition function, and found it is comparable in accuracy and precision to traditional methods for gas-phase molecules. This provides a new approach to solve the thermodynamics and kinetics questions in real catalytic systems.
Chapter 8

Summary and Future Direction

Converting carbon-containing compounds to valuable chemicals and fuels in an efficient and environmentally friendly manner, is one of the great challenges of the 21st century. Propene is the one of the most valuable chemicals and fuel in the petrochemical industry, being the raw material for a wide variety of commodity chemicals ranging from plastic products to gasoline components. Traditionally, the propene can be produced by steam cracking of hydrocarbons, refinery fluid catalytic cracking (FCC) or propane dehydrogenation. However, these processes either require much energy or produce propene with low yield and much waste. Considering these drawbacks of traditional processing routes, we focused on two promising catalytic conversion routes for propene production: 1) Metathesis of ethene and 2-butene, which is solvent-free, generates little waste, and requires low catalyst loads; 2) Methane dehydrogenation and CO₂ hydrogenation to methanol for use in the MTO process, where greenhouse gases are utilized to close the carbon cycle.

For metathesis of ethene and 2-butene, we investigated the initiation of olefin metathesis on tungsten trioxide (WO₃) catalysts, by showing that 2-butene more readily forms W-carbene active sites on the surface, compared to ethylene. We presented our analysis of the propagation steps at these active sites. The computed optimized structures and energetics of the reaction intermediates and products of propagation were obtained.

For CH₄ dehydrogenation, we modeled both (hemi)spherical and tetrahedral platinum nanoclusters. We showed that hydrogen production from methane would proceed at a higher rate and conversion on tetrahedral clusters than on hemispherical clusters. We further study
the support effect on reactivity of cluster for methane dehydrogenation. Both stoichiometric and reduced ceria do facilitate methane adsorption and dehydrogenation, as compared to unsupported clusters; an analogous β-silica support does not significantly enhance methane adsorption. We propose that the low-coordinated Pt sites and oxygen vacancies at the metal-support interface, along with lower activation strain on the supported catalysts, all contribute cooperatively to the enhanced catalytic activity. Our results confirm the critical role of support structure and composition for catalytic methane activation and dehydrogenation on noble metal clusters.

For CO\textsubscript{2} adsorption, we showed that it is thermodynamically favorable on reduced ceria (110) surfaces over the corresponding adsorption on stoichiometric ceria (110). Structural changes in the CO\textsubscript{2} molecule are also observed upon adsorption. At the split vacancy on reduced ceria, the molecule bends out of plane to form a unidentate carbonate with the remaining oxygen anion at the surface. For CO\textsubscript{2} hydrogenation to methanol, we built the reaction network including all possible intermediates, then simplified the network by stability and barrier analysis. Our results showed that carbine diol, formic acid and methynol are not feasible due to the high formation energy. Also, direct formyl hydrogenation to formaldehyde (H\textsubscript{2}CO), the key intermediate for methanol synthesis, is not feasible due to the high activation barrier. Instead, we find that H-formalin to formaldehyde is kinetically more favorable. The formaldehyde then converts into methoxy H\textsubscript{3}CO rather than H\textsubscript{2}COH, followed by a consecutive hydrogenation step to form methanol. Thus, two reaction channels to methanol are identified (i) COOH pathway via a carboxyl intermediate and (ii) HCOO pathway via a formate intermediate.

In addition, we developed three computational methodologies to study the two promising catalytic routes for propene production across a range of length and time scales. First, we investigated the effect of electronic structure on the properties and reactivity of these catalyst systems by computed the partial electronic density of states, electronic localization function and excess spin density. We applied this computational methodology to the study of methane activation and found faceted particles with more electrons in edge and vertex sites may facilitate CH\textsubscript{4} dehydrogenation. We also applied this method to the study of carbon dioxide activation and found that redox supports (e.g., reduced ceria with oxygen vacancy) can promote electron transfer reactions to activate the adsorbed CO\textsubscript{2}. Second, we developed a non-equilibrium thermodynamics approach to calculate energies of activation at finite
temperatures and rate constants, based on DFT barriers and the modified Bronsted-Evans-Polanyi principle. We applied this computational methodology to the study of metathesis propagation on WO$_3$ catalysts and CO$_2$ hydrogenation on reduced ceria. Third, we developed an approach to numerically compute heat capacities and other thermodynamic properties on extended catalytic systems based on the vibrational frequency results from DFT and the partition function. We applied this approach to the study of carbon dioxide hydrogenation and found it is comparable in accuracy and precision to traditional methods that have been well-developed for gas-phase molecules.

To summarize, in this thesis, we investigated the catalytic conversion of carbon-containing compounds into valuable chemicals and fuels by computational approaches based on density functional theory, and gained mechanistic, thermodynamic and kinetic insight into the elementary steps that comprise larger reaction networks. Ultimately, these theoretical findings and computational predictions can be used to guide experimental design, synthesis, and characterization of new catalyst systems.

A future direction for this work is to develop a complete microkinetic model for CO$_2$ hydrogenation at different operating condition. The microkinetic approach is attractive and appealing since it is not based on any arbitrary assumption on rate-determining step, and thus it is not restricted to a particular set of conditions. We have derived a complete set of elementary reactions (Table 7.4) and reaction routes with a known set of species (Figure 7.4), coupled with a reliable estimation of the elementary reaction energetics on reduced ceria catalyst based on DFT barriers and the modified Bronsted-Evans-Polanyi principle. The complete set of elementary reactions can be reduced using quasi-equilibrium and quasi-steady state approximations. The mathematical description of the reduced reaction network can generate a set of ordinary differential equations (ODE). Then the system becomes a set of differential algebraic equations that can be solved numerically using commercially available packages (e.g., MATLAB). Hence, a complete microkinetic model can show the temporal evolution of each species as a function of temperature and the partial pressures of molecules, such as CO$_2$ and CO, which would be of great significance in predicting the selectivity and yield of this process and guide experimental design of new catalysts.
References


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