# THEORETICAL AND EXPERIMENTAL STUDY OF BIMETALLIC CATALYSTS IN HETEROGENEOUS CATALYSIS AND ELECTROCATALYSIS FOR ENERGY APPLICATIONS

by

MyatNoeZin Myint

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

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### ABSTRACT

In this dissertation, non-precious bimetallic heterogeneous catalysts and electrocatalysts with specific functionality are studied for sustainable energy applications. It is demonstrated that through the combination of theoretical and experimental techniques, more active, selective and stable precious-metal-free bimetallic catalysts are identified for biomass-derived oxygenate reactions, reduction of CO<sub>2</sub> with ethane, and the hydrogen evolution/oxidation reaction (HER/HOR) in alkaline medium.

First of all, the adsorption and reaction of C3 oxygenates on Ni- and Mo-based bimetallic surfaces are investigated via density functional theory (DFT) calculations, temperature programmed desorption (TPD), and high resolution electron energy loss spectroscopy (HREELS). Propanal and 1-propanol are used as probe molecules for biomass-derived oxygenates due to their relatively high vapor pressures which can be introduced into ultrahigh vacuum (UHV) systems easily. The Vienna *Ab-initio* Simulation Package (VASP) is used in this work mainly to calculate the binding energies and the adsorption geometries of oxygenates and reaction intermediates, and to calculate the vibrational spectra of adsorbates on the catalytic metal surfaces. The trends established from DFT are correlated with the activity and selectivity determined experimentally from TPD, and the bond scission mechanisms are examined through HREEL spectra.

On Ni(111), Fe/Ni(111) and Cu/Ni(111) surfaces, DFT calculations predict that the binding energy trend of propanal and 1-propanol is Fe/Ni(111) > Ni(111) >

Cu/Ni(111). For propanal, the highest reforming and total activity are observed on Ni(111), while modifying the Ni(111) surface with Fe results in the highest decarbonylation activity to produce gas-phase ethylene. Depositing monolayer (ML) of Cu on Ni(111) leads to the highest total decomposition activity. Different 1-propanol decomposition reaction mechanisms are achieved on the three surfaces studied. Briefly, HREEL spectra show that on Ni(111) 1-propanol undergoes a selective dehydrogenation pathway to produce propanal, while on both bimetallic surfaces 1-propanol favors a non-selective total decomposition pathway to produce CO,  $H_2$  and surface hydrocarbons.

Next, the bimetallic modification effect of a single layer of Ni and Co on Mo(110) on the bond scission of C3 oxygenates is also studied. DFT results predict that the binding energy trend of propanal and 1-propanol is Mo(110) > Co/Mo(110) > Ni/Mo(110). TPD and HREELS results show that for both molecules, Mo(110) shows a highly selective deoxygenation pathway towards C–O/C=O bond scission to produce propene, while bimetallic surfaces instead exhibit a higher activity for C–C and C–H bond scission. Among the three surfaces, Ni-modification leads to the highest selectivity for decarbonylation to produce ethylene and Co-modification results in the highest selectivity for reforming to produce syngas.

The second section of this dissertation is the study of catalytic activation of CO<sub>2</sub> using ethane on supported bimetallic catalysts. Steady-states catalytic performance is evaluated using a flow reactor with in-line gas chromatography. CO chemisorption and temperature programmed reduction (TPR) are used to characterize the supported catalysts synthesized from the incipient wetness impregnation (IWI) method. The catalysts evaluated include CoPt/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub>, NiMo/CeO<sub>2</sub> and FeNi/CeO<sub>2</sub>, and

all bimetallic catalysts achieved an enhanced stability, compared to the corresponding monometallic catalysts. Two distinct types of catalysts, which break the C–C bond via the dry reforming pathway and which selectively break the C–H bond via the oxidative dehydrogenation pathway, are identified. It is shown that CoPt/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub> and NiMo/CeO<sub>2</sub> favor the dry reforming of ethane to produce synthesis gas, while FeNi/CeO<sub>2</sub> is a promising selective oxidative dehydrogenation catalyst to produce ethylene, CO and H<sub>2</sub>O. DFT energy profiles investigated confirm the two distinct reaction pathways on CoPt(111) and FeNi(111).

Lastly, the combined approach of DFT prediction and experimental results is employed to screening and designing highly efficient electrocatalysts in alkaline electrolytes. By determining the activity of HER on a series of monometallic surfaces, it is shown that the HER exchange current density in alkaline solution can be correlated to the calculated hydrogen binding energy (HBE) on the metal surfaces via a volcano type of relationship. Such correlation suggests that the HBE can be used as a descriptor for identifying HER/HOR electrocatalysts in alkaline medium. As a direct extension of this design principle, precious-metal-free bimetallic (NiMo) and multimetallic (CoNiMo) electrocatalysts with enhanced activity are identified.

# Chapter 1

## INTRODUCTION

#### **1.1 Introduction to Catalysis**

Catalysis is a multi-disciplinary field of science with a wide scope of industrial applications. Since the breakthrough in industrial catalysis with the development of ammonia synthesis in 1908,<sup>1</sup> catalysis has played an indispensable role in chemical, petrochemical, and biochemical industries. Approximately 85-90% of the chemical industry processes use catalysts.<sup>2</sup> In homogeneous catalysis, catalytic processes take place in the same physical phase. In heterogeneous catalysis, the catalyst and the reactants are in separate physical phases and typically solids catalyze reactions of molecules in gas or solution phase. One of the major differences between the two types of catalysis is the ease of separation of the solid catalyst. In general, while simple separation methods such as filtration can be used in heterogeneous catalysis, more complicated methods such as distillation are required for homogeneous catalysis. Electrocatalysis, the study of catalysis in electrochemical environments, is a special case of catalysis involving oxidation or reduction by transfer of electrons. Compared to heterogeneous catalysis, electrocatalysis involves more complex phenomena, solidliquid interfacial effects, charge transfer, and solvated charges, in addition to significant deactivation due to enhanced metal dissolution and corrosion in the aqueous phase environments. Unless otherwise stated, all discussion in this thesis will be in reference to heterogeneous catalysis and electrocatalysis for renewable and sustainable energy applications, particularly biomass-derived oxygenate reforming, CO<sub>2</sub> activation, and hydrogen evolution/oxidation reactions in alkaline environments. Each application will be introduced briefly in the following sections.

The overall goal of catalysis is to significantly improve the catalytic activity, control the selectivity to the desired products, and enhance the stability under more severe reaction conditions. Specific catalyst optimization is critical to ensure that downstream catalytic processes are commercially attractive and environmentally friendly. Designing efficient catalytic materials involves a combination of knowledge of thermodynamics, reaction mechanisms and kinetics based on experimental and theoretical fundamental understanding of electronic properties and physical structures as shown in Figure 1.1.



Figure 1.1 Schematic of designing catalysts

#### **1.1.1 Sabatier Principle**

Sabatier principle, the most fundamental principle in catalysis, shows a volcano curve dependence of the rates or activities of various catalytic reactions with respect to the strength of adsorption of the molecules. The principle states that for the highest activity, the optimum binding, neither too strong nor too weak, is necessary, as shown in Figure 1.2. If the binding energy is too strong, the reactive intermediates act as a desorption barrier and poison the catalyst surface. In contrast, if the binding is weak, the reaction will be hindered since the molecule needs to undergo activated adsorption on the catalyst surface. Numerous examples of such volcano plots in heterogeneous catalysis and electrocatalysis have been established in literature by plotting experimentally obtained catalytic activity as a function of the binding energy of the adsorbates predicted from density functional theory (DFT) to predict catalyst activity, screen and design novel catalysts.<sup>3, 4, 5</sup>



Metal-Adsorbate Bond Strength

Figure 1.2 Schematic representation of Sabatier principle: volcano-type relationship

#### **1.2 Bimetallic Surfaces in Catalysis**

Bimetallic surfaces exhibit unique properties different from their parent metals due to geometric, electronic and synergistic effects.<sup>5,6</sup> Monolayer bimetallic structures (MBS) have only one atomic layer of admetal deposited onto a host metal, and can be generally categorized according to three different configurations: the surface monolayer, the subsurface monolayer, and the intermixed or alloy configuration. These monolayer structure can change from one configuration to another depending on substrate temperature and reaction conditions. For example, for the Ni/Pt bimetallic

systems, deposition at 300 K leads to the formation of the Ni-terminated surface monolayer, Ni-Pt-Pt(111), while deposition at 600 K results in the formation of the subsurface monolayer, Pt-Ni-Pt(111).<sup>5</sup> In the presence of 0.5 ML of adsorbed O atoms, oxygen will induce segregation of subsurface Ni from Pt–Ni–Pt(111) to form thermodynamically more stable Ni-terminated surface.<sup>5</sup> Unique and improved catalytic activities of bimetallic surfaces have been reported for a variety of reactions including, but not limited to, reforming of oxygenates, hydrogenation of C=C and C=O bonds, dehydrogenation of N–H and C–H bonds, and CO<sub>2</sub> activation. Similarly, novel bimetallic catalysts have also been identified as highly efficient electrocatalysts for applications in fuel cells and electrolyzers.<sup>7</sup>

#### **1.3** Bimetallic Catalysts for Biomass Conversion

The use of bimetallic catalysts has been considered a promising route for biomass feedstock upgrading into sustainable chemicals and fuels. Unlike petroleum which is underfunctionalized, biomass is overfunctionalized and requires the removal of oxygen without reducing the carbon chain. The review of bimetallic surfaces for biomass conversion can be found in many papers.<sup>5, 6, 8, 9</sup> Among the several reactions involving lignocellulosic biomass conversion and upgrading such as hydrogenation, hydrogenolysis, oxidation, the focus of this work is on the reforming reaction via the C–C bond scission and the deoxygenation reaction via the C–O/C=O bond scission of oxygenates on non-precious bimetallic surfaces.

# 1.3.1 Reforming of Oxygenates

Oxygenated compounds are chemical compounds which contain oxygen in their chemical structures. Oxygenates derived from renewable biomass, particularly

lignocellulosic biomass, typically have low toxicity. Lignocellulosic biomass is widely available as low-cost feedstocks without competing with food sources. Examples of small oxygenates include methanol, ethanol and ethylene glycol, and large oxygenates include glucose, and sorbitol, *etc.* Among various industrially significant oxygenate reactions, the reforming of oxygenates is particularly important for two major reasons: for hydrogen production in fuel cells applications and for syngas production in upgrading feedstocks into chemicals and fuels via Fischer-Tropsch (FT) synthesis. In addition, the reforming of biomass-derived oxygenates is potentially considered a carbon-neutral process since  $CO_2$  released during biomass conversion can be used in the growth of biomass.

Reforming reaction occurs via the cleavage of C–C, C–H and O–H bonds to produce CO and H<sub>2</sub>, known as synthesis gas or syngas.

$$C_n H_{2y} O_n \leftrightarrow nCO + yH_2 \tag{1.1}$$

Reforming of small oxygenates on transition metal bimetallic surfaces have been studied in the ultrahigh vacuum environments and the activities have been correlated with the binding energy trends predicted from DFT.<sup>5, 6</sup> For example, on the Ni/Pt bimetallic surfaces, the binding energies of small oxygenates increase as the surface *d*-band center shifts closer to the Fermi level, and the reforming activity correlates well with the surface *d*-band center. The volcano relationship for the reforming yield as a function of surface *d*-band center of bimetallic surfaces has been suggested using methanol as a probe molecule on the Co/Pt and Ni/Pt bimetallic surfaces.<sup>10</sup> Similar reforming trends have been reported upon preparing Ni/Pt bimetallic surfaces on a Pt polycrystalline substrate, confirming the feasibility of extending the surface chemistry on the Pt(111) surface to the polycrystalline Pt foils, which contain both the (111) and

(100) crystal planes in order to bridge the materials gap. Reactor studies for several types of reforming – aqueous, steam and autothermal – have been extensively studied in order to bridge the pressure gap.<sup>6,8</sup>

Among various oxygenates, glycerol represents a very attractive feedstock for hydrogen production. Glycerol is non-toxic, nonflammable and biodegradable and typically prepared from sorbitol via hydrogenolysis and from glucose via fermentation. In contrast to starch-derived ethanol, glycerol is also a by-product in biodiesel production via transesterification of animal fats or vegetable oils using methanol and a base catalyst such as NaOH. Approximately 0.1 kg of glycerol is produced per kg of biodiesel. As biodiesel production has increased,<sup>11</sup> an efficient upgrading of glycerol is necessary. Glycerol reforming on different catalytic systems has been reviewed recently.<sup>11</sup>

$$C_{3}H_{8}O_{3} + xH_{2}O + yO_{2} \rightarrow aCO_{2} + bCO + cH_{2}O + dH_{2} + eCH_{4}$$
(1.2)

Most widely used glycerol reforming catalysts include precious metal catalysts such as Pt, Ru and Rh catalysts and non-precious metal catalysts such as Ni and Co on different supports. Despite its ability to break the C–C bond in the steam reforming reaction, Ni catalysts suffer from catalyst deactivation due to carbon deposition and sintering under reaction conditions. Various Ni-based bimetallic catalysts have been investigated and shown to improve the catalytic stability.<sup>12</sup>

#### **1.3.2** Deoxygenation of Oxygenates

Another important oxygenate reaction on transition metal catalysts is the deoxygenation reaction via the C–O/C=O bond scission to produce alkenes. Since biomass is composed of long-chain oxygen rich molecules, in order to increase the energy density, oxygen can be removed selectively via deoxygenation without reducing

the carbon chain length. Molybdenum carbide (Mo<sub>2</sub>C) catalysts have been shown to be a promising catalyst for the C–O/C=O bond scission based on the UHV studies of oxygenates. Upon extending into catalytic flow reactor studies, however, while Mo<sub>2</sub>C catalysts are very selective for the bond scission of the C=O bond in furfural, the catalysts suffer from significant deactivation.<sup>13</sup> In addition to carbide catalysts, nonprecious bimetallic catalysts such as FeNi/SiO<sub>2</sub> has also been shown to selectively cleave the C=O bond in furfural.<sup>14</sup>

## **1.4 Supported Bimetallic Catalysts**

Supported catalysts play an essential role in many industrial processes particularly refinery and the chemical industries. Catalyst supports are generally used to achieve high metal dispersion and stabilization of the active metals, and enlargement of the specific surface area. For instance, high dispersion ensures that a small amount of metal loading as low as 0.5 % on supports is still highly active, hence reducing the cost. Typical catalyst supports include Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, SiO<sub>2</sub>, MgO, CeO<sub>2</sub>, activated carbons and zeolites. It should be noted that supports often regarded as inert during reactions, depending on the reactions, the supports, particularly strong metal-support interaction (SMSI), can alter the catalytic properties of the active phase, thereby affecting the activity and/or selectivity. Clearly, while establishing trends of bond scission and reaction mechanisms on model surfaces is relatively simple, it is much more difficult for supported catalysts.

Section 1.4.1 and 1.4.2 will focus on the use of supported bimetallic catalysts for catalytic activation of CO<sub>2</sub> using hydrogen and ethane.

#### **1.4.1** Catalytic CO<sub>2</sub> Reduction with Hydrogen

Utilization of  $CO_2$  as a feedstock has been in the spotlight of research by the catalysis community in order to mitigate the  $CO_2$  atmospheric levels, and to produce economic and environmentally friendly value added intermediates and chemicals. However, low reactivity and thermodynamic stability of  $CO_2$  have hindered the large-scale commercialization.  $CO_2$  can be catalytically converted into CO via the reverse water-gas shift (RWGS) reaction shown in Equation 1.3.

 $CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)} \Delta H^{\circ}_{25} = 41 \text{ kJ/mol} \Delta G^{\circ}_{25} = 28 \text{ kJ/mol}$  (1.3) The endothermic nature of the reaction requires relatively high temperatures and an inexpensive hydrogen source in order to reduce the carbon footprint. It has been shown that both the metal and the support play an important role the RWGS reaction. Specifically, the active metal is reported to be important for controlling the selectivity, while the oxide support is responsible for improving the activity.<sup>15</sup> Among various oxide supports, CeO<sub>2</sub> is commonly used as a support for its ability to shift easily reduced and oxidized states which help accommodate during CO<sub>2</sub> dissociation. In addition to precious and non-precious supported metal catalysts, transition metal carbides (TMC) have also been studied for the RWGS reaction.<sup>16</sup> Reaction mechanisms involving catalytically activating CO<sub>2</sub> using hydrogen have been reviewed.<sup>17</sup>

#### **1.4.2** Catalytic CO<sub>2</sub> Reduction with Ethane

An alternative route to catalytically activate  $CO_2$  to produce syngas ( $CO + H_2$ ) is to use light alkanes such as methane and ethane. While the so-called dry reforming of methane to produce syngas is highly energy intensive, the reaction temperature can be lowered by about 100 °C upon using ethane instead, thereby lowering the energy requirement.<sup>18</sup> In addition to dry reforming of ethane, the alternative reaction pathway

of  $CO_2$  + ethane leads to the formation of ethylene, an essential basic material in the chemical and petrochemical industries, via the oxidative dehydrogenation pathway. At sufficiently high temperature, both reactions can occur simultaneously and hence it is important to identify catalysts which can selectively control the C–C bond scission in reforming and the C–H bond cleavage in the oxidative dehydrogenation reaction.

## 1.5 Hydrogen Evolution/Oxidation Electrocatalysis

Integrating hydrogen into the energy infrastructure is a viable solution to the global energy problem as hydrogen is considered a clean fuel of the future. Currently, hydrogen is mostly produced from fossil fuels such as natural gas, oil and coal via highly energy intensive steam reforming of methane. A hydrogen based system which consists of a combined used of electrolyzer and fuel cell is shown in Figure 1.3. This so-called hydrogen cycle generates and utilizes hydrogen without emission of pollutant gases or consumption of fossil fuels. Electrolysis of water generates highly pure CO<sub>2</sub>-free hydrogen, which can be directly used in fuel cells to produce heat and electricity. Water produced as by-product from fuel cells can be used in electrolyzers for splitting. Electrolysis of water enables large-scale hydrogen production with typical efficiencies of approximately 70-80%.



Figure 1.3 Schematic of the so-called hydrogen cycle

Both commercially available electrolyzers and fuel cells operate in either acidic or basic conditions. Although the cost of electrocatalysts comprises only a small percentage (approximately less than 13 %),<sup>19</sup> large-scale commercialization of these devices has long been hindered by the need for the precious metals such as platinum and ruthenium which are not only extremely expensive but also scarce. Many studies have sought to identify highly efficient, stable and cost-effective catalysts. As an alternative to low temperature proton-exchange membrane fuel cells (PEMFC) which operate in acidic conditions, alkaline or alkaline membrane fuel cells (AFCs/AMFCs) have been studied since the alkaline nature of hydroxide exchange membranes enables the utilization of earth-abundant non-precious metal catalysts. However, the slower kinetics of the hydrogen evolution/oxidation reaction (HER/HOR) even on the most active Pt catalyst in alkaline compared to that in acidic media hinders the development of these low temperature alkaline electrochemical devices. Enhancement of the cell efficiency therefore requires design and development of highly active electrocatalysts for the HER/HOR in alkaline electrolytes. Section 1.5.1 will focus on the reactions in alkaline conditions.

# 1.5.1 Hydrogen Evolution/Oxidative Reaction (HER/HOR) in Alkaline Medium

Electrochemical hydrogen evolution reaction (HER) is the most widely studied classical reaction in electrocatalysis, both experimentally and theoretically. The HER in base proceeds in the following sequence of Volmer-Heyrovsky or Volmer-Tafel mechanisms:

Volmer: 
$$H_2O + e^- + * \leftrightarrow H_{ad} + OH^-$$
  
Heyrovsky:  $H_{ad} + H_2O + e^- \leftrightarrow H_2 + OH^- + *$   
Tafel:  $2H_{ad} \leftrightarrow H_2 + 2*$ 

Similarly, the hydrogen oxidation reaction (HOR) in an alkaline medium proceeds through the following reactions by either Tafel-Volmer or Heyrovsky-Volmer squences:

Tafel: 
$$H_2 + 2^* \leftrightarrow 2H_{ad}$$
  
Heyrovsky:  $H_2 + OH^- + * \leftrightarrow H_{ad} + H_2O + e^-$   
Volmer:  $H_{ad} + OH^- \leftrightarrow H_2O + e^- + *$ 

Recent efficient electrocatalysts development of the HER in alkaline conditions has been reviewed.<sup>20</sup> As demonstrated by previous studies, the HOR activity in base on the most active catalyst, Pt, is two orders of magnitude smaller than in acid, which in turn requires higher Pt loading on the anode.<sup>21, 22</sup> Although PtRu alloy has been found to have enhanced HOR activity over Pt in a recent study,<sup>23</sup> the discovery of highly active non-precious HOR electrocatalysts in base is crucial in order to make AFCs/AMFCs practical. Ni-based materials are the most commonly used non-precious metal electrocatalysts for H<sub>2</sub> production in alkaline electrolyzers and the HOR in AFCs.

Several Ni-based bimetallic catalysts have been developed to increase the HOR activity. However, the enhancement of the HOR on Ni alloy over that on Ni is very limited, and the mechanism behind the improvement has been vague.

#### **1.6** Scope of Dissertation

This dissertation consists of 8 chapters. Chapter 2 gives a brief overview of the ultrahigh vacuum (UHV) chambers and the fundamental principles of surface science techniques used in this dissertation to prepare and characterize bimetallic model surfaces. Specifically, physical vapor deposition (PVD), Auger electron spectroscopy (AES), Temperature programmed desorption (TPD), and high resolution electron energy loss spectroscopy (HREELS) are discussed. To further extend surface science studies into more realistic catalytic reactor evaluation, this chapter then expands into an overview of a flow reactor setup, synthesis and characterization of supported catalysts. Chapter 3 focuses on a general background of density functional theory (DFT), its utilities and limitations.

The results from the Ph.D. research are divided into four chapters, from chapter 4–7. Chapter 4 discusses the adsorption and reaction of propanal and 1-propanol on Ni(111), Fe/Ni(111) and Cu/Ni(111) surfaces using DFT, TPD and HREELS as probe reactions for oxygenate reactions on non-precious metal surfaces. The adsorption geometry and trends in binding energy of propanal and 1-propanol are correlated with the activity and selectivity of C3 oxygenates on Ni(111), Fe/Ni(111) and Cu/Ni(111).

Chapter 5 will expand the study of the reactions of C3 oxygenates to Mo-based bimetallic surfaces. Particularly, the bond scission of C–O/C=O, C–C and C–H from propanal and 1-propanol on Mo(110), Ni/Mo(110) and Co/Mo(110) is studied. It will be shown that the bond scission activity and selectivity of small oxygenates can be tuned

upon admetal modification of Mo(110) and this result can be extended for more complex biomass-derived oxygenate platform molecules.

Chapter 6 discusses the catalytic conversion of CO<sub>2</sub> using ethane into a useful feedstock (synthesis gas) and a value-added monomer (ethylene) via the dry reforming (DRE) pathway through the C–C bond scission and the oxidative dehydrogenation (ODEC) pathway through the C–H bond scission, respectively. Results from this chapter identify CoPt/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub>, and NiMo/CeO<sub>2</sub> as reforming catalysts to produce syngas, and FeNi/CeO<sub>2</sub> as an oxidative dehydrogenation catalysts to produce supported by DFT calculations of energetics for the DRE and ODEC pathways over CoPt and FeNi surfaces.

Chapter 7 focuses on identifying non-precious metal electrocatalysts with high activity in alkaline electrolytes to produce  $CO_2$ -free hydrogen, which can be used for  $CO_2$  activation, instead of direct utilization of hydrocarbons. A volcano relationship is established between the calculated hydrogen binding energy (HBE) and the HOR/HER exchange current densities. Using this design principle, bimetallic NiMo and multimetallic CoNiMo catalysts are identified as highly active electrocatalysts. HBE predictions by DFT are also confirmed experimentally through H<sub>2</sub>-TPD.

Finally, Chapter 8 summarizes the major results in each chapter from this dissertation and includes proposed suggestions for future work.

# Chapter 2

## **EXPERIMENTAL METHODS**

#### 2.1 Introduction

The surface science experiments were carried out in the ultrahigh vacuum (UHV) chambers. The UHV techniques used in this dissertation were Auger electron spectroscopy (AES) to characterize the surface composition, mass spectrometry (MS) and temperature programmed desorption (TPD) to analyze the gas-phase products from surface reactions and to determine the mechanisms of surface reactions, and high resolution electron energy loss spectroscopy (HREELS) to detect the reaction intermediates based on the vibrational spectra of the adsorbates. These techniques are critical for fundamental molecular-scale studies of the reactions of oxygenates on well-characterized model surfaces in order to better understand the bond scission mechanisms and to identify potentially more active and selective catalysts.

The model systems used in this work were single crystal surfaces with the most thermodynamically stable facet such as (111) for face-centered cubic, (110) for bodycentered cubic, and (0001) for hexagonally-closed packed crystals. While model surfaces remove complexities such as support effects, dispersion, particle size and promoters, these surfaces represent the dominant plane of nanoparticles and can be used for fundamental studies. However, in order to address the "pressure gap and materials gap", which is associated with the use of model systems under well controlled UHV environments, more complex and industrially relevant supported catalysts were synthesized using the incipient wetness impregnation (IWI) method and the catalytic performance was evaluated using a flow reactor under atmospheric pressure for  $CO_2$  activation with ethane.

In this chapter, both UHV and reactor evaluation techniques will be discussed. The experimental details such as admetal deposition using physical vapor deposition (PVD) in the UHV chambers as well as supported catalyst characterization via CO chemisorption and temperature programmed reduction (TPR) will also be discussed. More details about synthesis and characterization of bimetallic surfaces as well as supported catalysts can be found in several excellent reviews.<sup>6, 24</sup>

### 2.2 Ultrahigh Vacuum (UHV) Chambers

The ultrahigh vacuum (UHV) chamber used for TPD study is a two-level stainless steel chamber and a top-down schematic of the chamber is shown in Figure 2.1. It has a base pressure of  $1 \times 10^{-10}$  Torr equipped with two metal sources for metal deposition, several leak valves for introducing reactants into the chamber, an ion sputter gun for surface cleaning, a single-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES) for surface characterization, and a quadrupole mass spectrometer (QMS) for TPD experiments. The single crystal can be moved in x, y and z directions and rotated 360 degrees around  $\theta$  axis using a sample manipulator in the chamber.

A separate three-level UHV system was used for the high resolution electron energy loss spectroscopy (HREELS) experiments, as described previously.<sup>25</sup> The base pressure is also maintained at  $1 \times 10^{-10}$  Torr and the chamber is equipped similarly to the TPD chamber, with the addition of LK3000 double-pass HREELS spectrometer in the bottom level. In general, the base pressure of the chamber needs to be maintained at  $1 \times 10^{-10}$  Torr or lower to ensure the cleanliness of the adsorbate-free crystal over the course of experiments since atmospheric or higher pressure environments lead to the complete coverage adsorption, almost instantaneously, as predicted by the kinetic gas theory.



Figure 2.1 Top-down schematic of UHV chamber used for temperature programmed desorption experiments. From Skoplyak<sup>26</sup>

#### 2.2.1 Admetal Deposition via Physical Vapor Deposition (PVD)

Physical vapor deposition (PVD) is the most common technique to prepare welldefined bimetallic surfaces. Among various PVD methods, in this dissertation, thermal evaporation was used. A metal overlayer is deposited on the well-ordered single crystal surface via the line of sight thermal evaporation of a highly pure admetal (99.9999+%)as shown in Figure 2.2. The metal source is prepared by wrapping 0.05 - 0.1 mm admetal wire around 0.2 - 0.5 mm tungsten (W) or tantalum (Ta) wire, which is then coiled and connected to DC power supply through two copper feedthroughs for resistive heating. The admetal has to be resistively heated to near melting temperature to create a flux of atoms. Refractory metals such as W and Ta are most commonly used for their high melting points during resistive heating in order to avoid contamination during deposition. The deposition is controlled via the heating current, the deposition time, and the substrate temperature. A lower heating current could lead to longer deposition time, which can results in the adsorption of impurities from the background on the crystal surface during deposition. A higher heating current can often result in metal source rupture. The substrate temperature, the temperature at which the single crystal is maintained during deposition, can affect the structures of bimetallic surfaces such as surface monolayer, subsurface monolayer and intermixed bimetallic surfaces.<sup>5</sup> In this work, the substrate temperature is maintained at 300 K to prepare surface monolayer structures.

While evaporation is a simple process to prepare highly pure monolayer bimetallic surfaces relatively inexpensively, the line of sight where atoms travel in straight lines can result in poor surface coverage. Other limitations of the evaporation method include the selection of admetals which need to be pure and easy to deposit.
Alloy admetals are typically not ideal for deposition since they have different melting points.



Figure 2.2 Schematic diagram of line-of-sight physical vapor deposition through thermal evaporation of filaments. Revised from the review by Chen *et al.*<sup>5</sup> Copyright © 2008 Elsevier Ltd.

## 2.2.2 Auger Electron Spectroscopy (AES)

Auger electron spectroscopy (AES) is a widely used surface sensitive technique to determine the composition of the surface layers of a sample. The AES process, also known as a three-electron process, is shown in Figure 2.3. Briefly, a core hole is created in the inner (K) state when a beam of high energy electrons, typically 3–5 keV, is exposed to the sample. The vacancy is then filled by the relaxation of an outer higher level shell ( $L_1$ ) electron in order to maintain the low energy stable state. The available excess energy liberated by this relaxation is simultaneously transferred to another outer shell ( $L_{23}$ ) electron, which causes the electron to be ejected beyond the vacuum level and detected by the analyzer. This emitted electron is called the Auger electron and has a characteristic kinetic energy. Hence each element, from Li and higher, generates a characteristic spectrum of peaks at various kinetic energies. It is important to note that since AES process requires at least three electrons to be present, it has the lower limit of Li, excluding H and He. AES spectra are usually recorded in the differential dN(E)/dE mode to obtain a better sensitivity for detection by extracting the contribution from a continuous background data from the secondary electrons.

The peak-to-peak height of differentiated auger peaks is proportional to the surface concentration. However, a higher peak does not mean a higher concentration since the sensitivity factor needs to be taken into account. The details on how to determine the thickness of admetal on the substrate and the growth mechanism of the metal overlayer based on the AES peak intensity can be found in these reviews.<sup>5, 6</sup>



Figure 2.3 Schematic illustration of the AES process

In addition to AES, X-ray photoelectron spectroscopy (XPS) can also be used as a surface analysis technique. While both techniques are elemental specific, they use different mechanisms of operation; AES uses a beam of primary electrons and XPS uses X-rays to impinge upon the sample. As mentioned previously, AES is a three-electron process while XPS is a single-electron process. Furthermore, although AES is relatively insensitive to the chemical state (i.e. oxidation state) of metals, it is more sensitive for low atomic number atoms and has high spatial resolution.

## 2.2.3 Temperature Programmed Desorption (TPD)

Temperature programmed desorption (TPD) is used for the qualitative and quantitative analysis of the gas-phase products from surface reactions under UHV conditions. Specifically, TPD experiments provide information regarding the desorption products and their desorption temperatures which can be used to identify the reaction mechanism of the molecules of interest on the single crystal catalyst surface. Briefly, TPD experiments are performed by dosing the molecule into the chamber while the crystal temperature is maintained at low temperature, typically 110 - 145 K, to allow for enhanced adsorption of the molecule on the crystal surface. The surface is then resistively heated at a constant rate at 3 K/s and the desorption species are monitored by a quadrupole mass spectrometer (QMS UTI-100C).

TPD spectra are obtained by plotting the intensity of masses detected by mass spectrometer as a function of temperature. The sample temperature at any given time T(t) can be approximated by

$$T(t) = T_0 + \beta t \tag{2.1}$$

where  $T_0$  is the initial temperature and  $\beta$  is a constant heating rate. Reaction products are identified by comparing detected masses with the standard fragments (typically from

NIST) and the peak areas are used in TPD quantification to determine the activity based on molecules reacting per surface atom. It is particularly important to differentiate the overlapping cracking patterns of different products to accurately identify the reaction products. Furthermore, the contributions from adsorbed  $H_2$  and CO from the UHV background needs to be adjusted for TPD quantification. The specific quantification methods are discussed in details in Chapters 5 and 6.

TPD peak shapes and temperatures at different coverages provide information regarding the kinetic order of a desorption process. If TPD peaks are asymmetric but the peak temperature is independent of the coverage, it is a first-order desorption process. On the other hand, if symmetric peaks and peak temperature shifts are observed, it is a second-order process. The shift in peak temperature in the later process is due to the change in the preferential binding sites and/or the interaction among adsorbates on the surface. Typically, a first-order desorption which indicates the presence of a single surface species occurs at low temperature, while a second-order desorption which indicates a surface recombination process occurs at high temperature. Physisorbed multi-layer desorption is independent of the surface coverage and it would follow zero-order desorption kinetics. In general, multi-layer desorption occurs at a low temperature of typically less than 150 K for molecules containing relatively small number of carbon and oxygen atoms, such as those used in this thesis.

It is also important to distinguish between reaction- and desorption-limited desorptions. In reaction-limited desorption, desorption of the gas-phase products occurs as soon as reaction is completed. Hence, TPD alone is sufficient to identify the stable reaction intermediates and consequently the reaction pathways since the activation barrier for reaction can be directly approximated. In contrast, in desorption-limited

desorption, the gas-phase products will remain on the surface even after the reaction until the temperature is high enough to either overcome the activation barrier for desorption or promote further reaction. In order to differentiate between reaction- and desorption-limited desorptions, the desorption temperature of the product species from the surface reaction should be compared with that of the same species in the absence of surface reaction, obtained from directly dosing it on the same surface. If the desorption temperature from the surface reaction is higher than that in the absence of the reaction, it is a reaction-limited desorption.

For an unactivated desorption, molecules travel from physisorption to chemisorption without requiring additional energy. In this case, the activation barrier for desorption is equal to the binding energy which can be correlated with the desorption peak temperatures from TPD experiments. The activation energy for desorption can be approximated using the Redhead equation shown below. <sup>27</sup>

$$-\frac{d\theta_A}{dt} = \beta \frac{d\theta_A}{dT} = \frac{r_d}{N_s} = k_0 \theta_A^n exp^{\left(-\frac{E_a}{RT}\right)}$$
(2.2)

where  $r_d$  is the desorption rate of species,  $N_s$  is the total number of surfaces sites,  $k_0$  is the rate constant for desorption,  $\theta_A$  is the coverage of the species A, n is the order of the reaction,  $E_a$  is the activation energy for desorption, R is the ideal gas constant, t is time and T is the absolute temperature.

## 2.2.4 High Resolution Electron Energy Loss Spectroscopy (HREELS)

HREELS is a surface sensitive technique used to detect the vibrational motions of atoms and molecules on or near the surface, thereby providing information regarding the reaction intermediates and the binding configurations of the adsorbates on the surface. The combined use of TPD and HREELS in surface science studies reveals the major aspects of the reaction products and the intermediates, important to identify the reaction mechanisms. HREELS is similar to infrared reflection adsorption spectroscopy (IRAS), except that the UHV condition in HREELS allows detection of vibrations in the "fingerprint region", typically less than 600 cm<sup>-1</sup>, which represents surface metal-adsorbate vibrations. The schematic of the HREELS process is shown in Figure 2.4. Briefly, when a low-energy monochromatic electron beam (generally 6 eV) is directed to the surface at an angle  $\theta = 60^{\circ}$ , the electrons are reflected off the surface at the same angle  $\theta$  and during reflection, some of the electron beam energy is lost as the vibrational modes of the surface and the molecules adsorbed on the surface.



Figure 2.4 Schematic illustration of the HREELS process

## 2.3 Reactor Studies

UHV techniques provide useful molecular understanding of model catalyst surfaces and reaction mechanisms, critical for designing catalysts with desirable activity, selectivity, and stability. However, the ideal UHV environment using the model surfaces creates the "pressure and materials gaps" and numerous efforts have focused on bridging the gaps in order to evaluate catalysts under more realistic conditions.<sup>6, 24</sup> The second half of this dissertation involves catalytic evaluation of the supported catalysts using flow reactor under atmospheric pressure.

## 2.3.1 Flow Reactor Setup

Designing an appropriate reactor for heterogeneous catalysis is vital to eliminate the heat and mass transfer effects as much as possible. For all experiments involving catalytic performance evaluation throughout this thesis, a fixed bed reactor is used for its relatively straightforward design and easily accessible sampling and analysis. Fixed bed reactors are typically used in the synthesis of large-scale basic chemicals and intermediates as well as treating harmful and toxic substances. Generally, flow reactor experiments are performed in a <sup>1</sup>/<sub>4</sub> inch quartz reactor located in a furnace under atmospheric pressure. An internal K-type thermocouple located just above the catalyst bed is used to monitor the reactor temperature. An additional thermocouple placed on the outside of the reactor is used to confirm the reactor set point temperature and its measurement is within 3–4 K of the reading from the internal thermocouple. The flow of reactant and diluent gases is controlled using Cole-parmer mass flow controllers and the pressure is recorded using an in-line pressure gauge (Omega). Approximately 100 mg of catalysts, sieved to 16–20 mesh, are reduced *in-situ* before the reaction at 450 °C for 1 h with a feed ratio of unity for H<sub>2</sub> and He (20 mL/min each). With the constant total flow rate at 40 mL/min, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and He as a diluent are introduced at 1:1:2 ratio into the reactor. The catalysts are heated to 600 °C and kept at this temperature for 12 h for steady-state measurements. Gas products are analyzed on-line using a gas chromatography (Agilent), equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD). TCD measures the changes in carrier gas thermal

conductivity caused by the presence of the sample. Typically, He or nitrogen is used as carrier gas for their high thermal conductivity. TCD has a low sensitivity and depends on flow rate and concentration. FID, on the other hand, is a most widely used detector due to its high sensitivity and low noise. It is also unaffected by flow rate. FID, however, requires a flammable gas and destroys the sample when the sample undergoes either pyrolysis or chemical decomposition at high temperature upon exposure to an air- $H_2$  flame. Ions produced from hydrocarbon decomposition are attracted to the collector which generates the signals based on the number of ions hitting the collector.

Calibration gas mixtures are used for construction of calibration curves for gas products. The concentration of each gas-phase species is obtained by correlating the peak area of the pure compound to its concentration in a calibration gas standard. Conversion and selectivity were defined as

$$Conversion = \frac{moles_{reactant}^{inlet} - moles_{reactant}^{outlet}}{moles_{reactant}^{inlet}} \times 100 \%$$

$$Selectivity_{i} = \frac{moles \ of \ carbon - containing \ product_{i}}{Sum \ of \ carbon - containing \ products} \times 100 \ \%$$

#### 2.4 Catalyst Synthesis

Supported catalysts are used in many industrial applications since the support provides high surface area and stabilizes the dispersion of the active component.<sup>1</sup> Typically, highly porous supports with high thermal stability and mechanical strengths are desired. Various methods to synthesize supported catalysts are discussed in details in the following review.<sup>6</sup> Monometallic and bimetallic supported catalysts in this dissertation are synthesized using incipient wetness impregnation method discussed below.

## 2.4.1 Incipient Wetness Impregnation (IWI)

All monometallic and bimetallic catalysts investigated in this dissertation were synthesized using incipient wetness impregnation (IWI) method, the most common synthesis technique in heterogeneous catalysis. Briefly, the support material is impregnated with an aqueous solution containing the active metal precursor. The volume of the aqueous metal precursor solution needs to be the same as the pore volume of a catalyst support in order to allow capillary action.<sup>28</sup> Upon adding the precursor solution dropwise to the support, this capillary action carries the aqueous solution up into the pores of the support, where the metal precursor is deposited within the pores and on the surface of the catalyst support. If the solution added is in excess of the support pore volume, slow migration due to diffusion occurs instead of a capillary action. The support pore volume can be measured via gravimetric method by saturating the support with deionized water and noting the weight increase. The amount of precursor depends on the desired metal loading although the maximum loading is limited by the solubility of the precursor in the solution. If high weight loadings of metals or support with very low pore volume are desired, an alternative slurry synthesis can be used.

The impregnated catalyst is then thermally treated by subsequent drying, calcination, and reduction. The catalyst is dried in air to eliminate solvent and to allow for precursor crystallite formation. The different rate of drying results in a varying distribution of metal precursors in the support.<sup>29</sup> At slow drying rate, the precursor metals concentrate towards the center of the pellet, resulting in an egg-yolk distribution.

At fast drying rate, on the other hand, deposition occurs near the pore entrances to form an egg-shell distribution. For uniform dispersion, mild drying rate is desirable.

The dried catalyst is then calcined to decompose the volatile precursor salt and to deposit the metal as an oxide on the support surface. Calcination ensures that the precursor salts do not re-dissolve in the presence of moisture, thereby maintaining the stable metal oxides on the catalyst support. The calcined catalyst is then reduced, typically in a mixture of hydrogen and helium, prior to reaction.

## 2.5 Catalyst Characterization

#### 2.5.1 CO Chemisorption

A pulse chemisorption analysis is widely used in heterogeneous catalysis to provide information regarding active metal surface area (AMSA) or the number of active metal sites and percent metal dispersion of catalysts.<sup>30</sup> AMSA is particularly useful for comparing the reaction data for different catalysts for a given reaction or for the same catalyst from different laboratories synthesized via a variety of procedures. AMSA can be used to calculate turn over frequency (TOF), which is defined as the number of molecules reacting per catalytic active site per unit time at the conditions of the experiments. Hence, TOF values typically represent intrinsic catalytic activity for a better comparison of the catalysts.

Different injected gases such as  $H_2$ ,  $O_2$ , CO, NO, and  $NO_2$  are commonly used for chemisorption analysis<sup>30</sup> and throughout this thesis, the CO uptake values are obtained using an AMI-300ip (Altamira). Briefly, the catalyst is reduced in the presence of  $H_2$ -containing gas mixture at a particular temperature. After reduction, the catalyst is cooled to room temperature, followed by pulsed CO flow over the catalyst. A thermal conductivity detector (TCD) is used to analyze the amount of CO flowing out of the reactor.

#### **2.5.2** Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) is used to determine the number of reducible species present on the catalyst surface and the temperature at which the reduction of each species occurs. TPR is most commonly used for characterization of metal oxides, mixed metal oxides and supported metal oxides to investigate the most efficient reduction conditions. Briefly, the catalyst is treated by flowing an analysis gas mixture of hydrogen and inert carrier gas (typically argon) at low temperature and then heated at a constant rate. TCD records the changes in the thermal conductivity of the effluent stream and the TCD signal is then converted to the amount of hydrogen consumed, which is plotted as a function of reduction temperature ( $T_{max}$ ) shows the temperature at which the maximum rate of reduction occurs. By comparing the peak temperatures, reducibility of different species can be determined; a higher  $T_{max}$  indicates a decrease in reducibility.

## Chapter 3

# **DENSITY FUNCTIONAL THEORY**

A fundamental understanding of reaction mechanisms in heterogeneous catalysis and electrocatalysis is crucial in developing new catalyst design strategies and made possible by increasingly efficient computational studies. The advancement of quantum mechanics, density functional theory (DFT) and other forms of computational chemistry, has helped identify descriptors of catalytic activity and selectivity of a variety of industrially important reactions. Numerous reviews have discussed recent developments and discoveries.<sup>31, 32, 33, 34</sup>

DFT was used in this work mainly to generate correlations to predict the catalytic behavior of ideal metal surfaces on an atomistic level. Establishing correlations and trends is particularly efficient compared to detailed kinetic studies and analogous experimental screening to design novel catalysts for desired activity and selectivity. Simulation of complex systems can be extremely computationally expensive since it involves building reaction networks based on the calculated binding energy and the activation barriers of many possible reaction intermediates on a variety of catalytic sites.

The main purpose of this chapter is to provide a brief introductory explanation about the most fundamental equations for DFT and general methods applied throughout this dissertation In addition, the application and limitations of DFT will also be discussed. A complete derivation of the techniques used in DFT or a full explanation of quantum mechanics calculations for reactions on solid surfaces is outside the scope of this dissertation. The interested reader is referred to several excellent review articles on this topic.<sup>35,36,37</sup>

#### 3.1 Introduction

Density functional theory (DFT), which solves for the ground-state electron density rather than individual electrons, provides an effective way to predict molecular and structural properties such as adsorbate binding energy, vibrational frequency and surface *d*-band center. Furthermore, DFT provides reliable predictions of structure, stability and reaction mechanisms, essential for exploring and understanding the catalytic properties. Briefly, DFT solves a set of time-independent one-electron Schrödinger equations (the Kohn-Sham equations), simplifying the complicated many-electron Schrödinger equation.<sup>38</sup>

## 3.1.1 The SCHRÖDINGER equation

The simple form of Schrödinger equation is

$$H\Psi = E\Psi \tag{3.1}$$

where *H* is the Hamiltonian operator,  $\Psi$  is a set of wave functions or eigenstates of the Hamiltonian and *E* is the ground-state energy of the electrons. Since ground-state energy is independent of time, this Schrödinger equation is known as the time-independent Schrödinger equation. In reality, multiple electrons are interacting with multiple nuclei, and thus the Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i=1}^{N}V(r_i) + \sum_{i=1}^{N}\sum_{j(3.2)$$

where m is the electron mass, N is the number of electrons. This equation can be explained as the sum of, in order, the electron kinetic energy, the interaction energy between electron and nucleus, and the interaction energy between different electrons. The electronic wave function  $\Psi$  can be approximated as a product of individual electron wave functions. However, individual electron wave functions  $\Psi_i(\mathbf{r})$  cannot be found separately; these wave functions are coupled and must be solved simultaneously. Hence, the Schrödinger equation is a many-body problem, which is computationally very difficult and expensive.

#### **3.1.2 Density Functional Theory (DFT)**

DFT eliminates the many-body problem by solving for the electron density instead of solving for the individual electrons based on two fundamental theorems, the Hohenberg-Kohn and the Kohn-Sham theorems. The Hohenberg-Kohn theorem states that the energy and the wave function of the ground-state can be uniquely represented by the functional of the ground-state electron density, which minimizes the total energy. In other words, once the ground-state electron density is known, all other ground-state properties will follow. To further simplify the equation, the Kohn-Sham theorem states that the electron density can be represented by solving a set of equations where each equation is a single-particle equation. The Kohn-Sham equations can be expressed as

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}) + V_H(\mathbf{r}) + V_{XC}(\mathbf{r})\right]\Psi\mathbf{i}(\mathbf{r}) = \epsilon_i \Psi\mathbf{i}(\mathbf{r})$$
(3.3)

This equation is similar to the Schrödinger equation except that there are no summations in the equation since each equation only involves a single electron, and the electronelectron interaction potential is now divided into the Hartree potential  $V_H(\mathbf{r})$ , which describes the electron-electron Coulomb repulsion, and an exchange-correlation potential,  $V_{XC}(\mathbf{r})$ . While the rest of the terms are the "known" terms, the exchangecorrelation potential,  $V_{XC}(\mathbf{r})$  needs to be specified in order to solve for the exact electron density.

#### **3.1.3** Exchange-Correlation (XC) Functionals

Local density approximation (LDA) assumes that the density can be locally treated as a uniform electron gas which is frequently used to calculate molecular geometries and vibrational frequencies. However, it must be noted that with LDA, bond energies are overestimated.<sup>35</sup> Modification of LDA leads to the use of generalized gradient approximation (GGA), which includes the density gradient in addition to the density. Some of the most widely used functionals for calculations of solid surfaces include the Perdew-Wang functional (PW91) and the Perdew-Burke-Ernzerhof functional (PBE). In addition, there are other more accurate hybrid DFT methods such as B3LYP which incorporates exact exchange energy (EXX) contribution. In this dissertation, the PW91 functional within the generalized gradient approximation (GGA) was used to approximate the exchange-correlation energy. It is important to specify which functional is used in the calculations since different functionals result in somewhat varying outcomes.

#### **3.2 DFT Implementation**

The commercially available DFT software package, the Vienna *ab-initio* simulation package (VASP) from the Theoretical Physics Department at the University of Vienna, was used for all calculations in this thesis. DFT was employed in this dissertation for two types of calculation: (1) adsorbate binding energy and adsorption geometry and (2) adsorbate vibrational frequencies on monometallic and bimetallic surfaces.

#### **3.2.1** Representation of Surface Models

Two most common models for simulations of the electronic structure of surfaces of crystalline solids are the cluster model and the slab model. In the cluster model, the surface is represented as a small isolated cluster of atoms by neglecting the effect of the surface atoms farther away from the adsorbates. Hence, the choice of cluster size and shape is essential to reduce the boundary effects. The slab model, on the other hand, treats the surface as a slab with a periodic structure along the surface, where the slab is infinite in two dimensions, but finite along the surface normal. Implementation of periodic boundary conditions reduces computation time and an infinite slab is commonly used to represent the single crystals used in UHV experiments. In this model, the choice of the vacuum thickness and the slab thickness is essential. In fact, to avoid the interactions between surfaces of consecutive slabs, the layer of vacuum needs to be large enough. To ensure the middle layer of the slab exhibits bulk-like properties, the layer of the slab needs to be thick enough. For all calculations in this work, the slab model with a periodic  $3 \times 3$  unit cell with four layers of metal atoms separated by six layers of vacuum was used.

#### **3.2.2** Basis Sets and Pseudopotentials

Two commonly used basis sets are localized functions and planewaves. Localized basis sets, also known as atomic basis sets, are centered on nuclei and some well-known examples include slater-types or Gaussian functions. These basis types are more widely used in the cluster model. Planewaves basis sets, mostly used in the slab model, are delocalized periodic basis functions where the convergence can be systematically enhanced by setting a cut-off energy. This truncation reduces the computational load and in this work, a basis set of plane waves up to an energy cut-off of 396–400 eV was used. Although the cut-off energy required to obtain a particular convergence precision is element dependent, this dissertation focuses on establishing the trend and hence the cut-off energy was kept constant in all calculations.

The computational time can be significantly reduced by reducing the number of planewaves needed. Puseudopotential approximation eliminates the core electrons which do not involve in bonding interactions and the oscillating behavior of the valence electrons by describing valence electrons via a smooth effective pseudowavefunctions. The pseudopoentials used in this dissertation were Vanderbilt ultrasoft pseudopotentials.

#### **3.2.3** Spin Polarization and k-points

Spin polarization calculations are used to describe the magnetism of itinerant electrons in solid state materials. Magnetism is caused by the nonzero spin of electrons. In general, if spin polarization is not explicitly included, calculations are faster. However, spin polarization calculations are particularly important for elements with magnetic moments such as Fe, Ni and Co. Spin polarization was used in all cases in this work.

Two most common schemes for generating k-points are the Chadi-Cohen and the Monkhorst-Pack schemes. The number of k-points affects calculation time and the convergence. While it is computationally efficient to reduce the number of k-points, it is important to choose a sufficiently dense k-point mesh to ensure convergence. For establishing trends in the same unit cell, the same k-point set should be used to cancel out the possible errors generated from a non-converged k-point sample. This dissertation used a  $3 \times 3 \times 1$  Monkhorst-Pack<sup>39</sup> grid, where only one k-point is used in the direction normal to the surface (z-axis) since there is no dispersion of the electronic band structure of the slab in the z-direction to sample. Thus, the k-point mesh lies in the xy plane.

#### 3.2.4 Vibrational Frequency Calculations

DFT can also be used to calculate vibrational spectra of small organic molecules that can be compared with the experimental IR or HREELS spectra to assisit interpretation and characterization. In DFT, vibrational frequencies are calculated around optimized equilibrium structures on the potential energy surfaces via the harmonic oscillator potential approximation<sup>35</sup> and hence it is important to perform frequency calculations after optimization. While in principle *ab initio* calculations can be used for vibrational analysis to desired accuracy, they do not account for anharmonicities of vibrational modes, leading to variations between the calculated and experimental results. More reliable predictions can be performed by optimizing functionals, scaling methods and basis sets.<sup>40</sup>

## 3.3 Limitations of DFT

While DFT is an efficient tool to predict the geometric and electronic structures of molecules and ideal surfaces, more complex catalytic systems are required to accurately account for the effects of realistic chemical environment such as support effects and change of surface chemical composition. At present, DFT limitations include inadequate predictions of the breaking of chemical bonds, the band gaps in semiconducting and insulating materials, charge transfer excitation energies, and molecular ions dissociation energies. Cohen *et al.*<sup>41</sup> attributed that such limitations are caused by lack of adequately accurate and universally applicable exchange-correlation functionals. Interested readers are encouraged to refer to the following recent perspectives on DFT.<sup>42, 43, 44</sup>

#### Chapter 4

# REACTION PATHWAYS OF PROPANAL AND 1-PROPANOL ON FE/NI(111) AND CU/NI(111) BIMETALLIC SURFACES

#### 4.1 Introduction

The generation of hydrogen from biomass-derived oxygenate compounds is a desirable and viable solution to a sustainable environment.<sup>8,45</sup> Glycerol, commonly referred to as an "alcohol sugar", is a byproduct in the biodiesel production and different types of glycerol reforming processes – steam, aqueous, and autothermal reforming – have been extensively studied.<sup>8,11</sup> However, finding an efficient and stable non-precious metal catalyst for hydrogen production from glycerol remains a great challenge.<sup>11</sup> Nickel, although an effective inexpensive oxygenate reforming catalyst due to its activity in C–C, C–H, and O–H bonds cleavage,<sup>46</sup> has lower selectivity to hydrogen production compared to the precious metal Pt catalyst.<sup>47</sup> To improve the catalytic selectivity and stability, Ni-based bimetallic catalysts have been investigated for oxygenates reforming.<sup>8,48, 5, 6</sup>

Due to the low vapor pressure of glycerol and difficulty in introducing it into ultrahigh vacuum (UHV) systems, fundamental surface science studies of new catalysts for glycerol have been limited. From the first attempt to study glycerol reforming on Ni/Pt bimetallic systems under UHV condition, Skoplyak, *et al.* have reported that glycerol shows the same reforming trends as smaller oxygenates such as ethanol.<sup>49</sup> Since propanol has been considered as a good surrogate molecule for glycerol,<sup>50</sup> in this work, 1-propanol has been studied as a model compound to investigate the reforming reaction

on Fe/Ni(111) and Cu/Ni(111) bimetallic surfaces. Another C3 oxygenate, propanal, is also studied to determine how the presence of the C=O bond affects the reaction pathway.

Previously, adsorption and reaction of 1-propanol and propanal have been studied under UHV conditions on Pt-group metals, particularly Rh(111),<sup>51</sup> Pd(111),<sup>52</sup> Pd(110),<sup>53</sup> and Pt(111).<sup>54</sup> Overall, aldehyde adsorption on metal surfaces can occur through either the oxygen lone pair in an  $\eta^1$  configuration or the carbonyl  $\pi$  orbital in an  $\eta^2$  configuration. The coordination geometry of aldehyde has been reported to be an important factor in determining the reaction pathways. On the other hand, the reactions of alcohol on metal surfaces can occur via a non-selective total decomposition pathway to produce CO, H<sub>2</sub> and surface hydrocarbons or via a selective dehydrogenation pathway where the O–H bond is cleaved first to form alkoxy, followed by the  $\alpha$ C–H bond cleavage to form aldehyde or ketone and then the  $\alpha$ C–C bond cleavage to form the corresponding products.<sup>55</sup> In addition to monometallic surfaces, reactions of propanal, 2-propenol, and 1-propanol – all hydrogenation products of acrolein – have been studied on Ni/Pt(111) bimetallic surfaces to understand different hydrogenation pathways of acrolein.<sup>56</sup> Both propanal and 1-propanol undergo mainly molecular desorption and decarbonylation to produce gas-phase ethylene on the monometallic and bimetallic surfaces.

The focus of this study is to investigate the reaction pathways and intermediates of propanal and 1-propanol on Ni(111), Fe/Ni(111) and Cu/Ni(111) surfaces from DFT and parallel TPD and HREELS experiments. We first present trends in the binding geometry and energy of propanal and 1-propanol, along with their corresponding reaction intermediates on Ni(111) and metal-modified Ni(111) surfaces. Reaction products are monitored through TPD and surface reaction intermediates are studied with HREELS.

## 4.2 Theoretical and Experimental Methods

# 4.2.1 DFT Calculations

Theoretical calculations were performed with the Vienna *Ab initio* Simulation Package (VASP). The exchange-correlation energy was approximated using the PW91 functional within the generalized gradient approximation (GGA) with a basis set of plane waves up to an energy cutoff of 396 eV. In all cases, the model surface consisted of a periodic  $3 \times 3$  unit cell with four layers of metal atoms at the corresponding most closed-packed configurations separated by six equivalent layers of vacuum. The two bottom layers of the slab were fixed while the top two layers and the adsorbate were allowed to relax to reach the lowest energy configuration. The Fe/Ni(111) and Cu/Ni(111) surfaces were modified by replacing all Ni atoms from the top layer with Fe or Cu atoms.

Propanal, 1-propanol, propionyl and propoxy were adsorbed on the atop sites of adjacent metal atoms. A low coverage (1/9 ML) was used to minimize the adsorbate-adsorbate interaction. For propanal and propionyl, both  $\eta^1$  and  $\eta^2$  configurations were considered. The aldehyde is bound through the O lone pair in the  $\eta^1$  configuration, and through both C and O atoms of the carbonyl groups in the  $\eta^2$  configuration. Binding energies were calculated using the equation:

$$BE_{ads/slab} = E_{ads/slab} - E_{slab} - E_{gas}$$

where  $E_{ads/slab}$  is the total energy of the slab with adsorbates,  $E_{slab}$  is the energy of the slab, and  $E_{gas}$  is the energy of the adsorbates in the gas phase. Only the values corresponding to the most stable configuration are listed in Table 4.1.

## 4.2.2 Preparation of Bimetallic Surfaces

The ultrahigh-vacuum (UHV) chamber used for TPD study is a two-level stainless steel chamber with a base pressure of  $1 \times 10^{-10}$  Torr equipped with Auger electron spectroscopy (AES) for surface characterization and a quadrupole mass spectrometer (MS) for TPD experiment. A separate UHV system was used for the high resolution electron energy loss spectroscopy (HREELS). The Ni single crystal sample is a (111) oriented, 1.50 mm thick disk (99.99%) with 8.00 mm in diameter. The crystal was spot welded directly to two tantalum posts which served as thermal contacts and electrical connections.

The Ni(111) surface was cleaned by repeated cycles of Ne<sup>+</sup> sputtering at 300 K and annealing at 1100 K. The surface was then modified by depositing 3*d* metals (Fe, Cu) using physical vapor deposition (PVD). The evaporative PVD doser consisted of a high purity Fe or Cu wire (99.9999+% from Alfa Aesar) wrapped around a tungsten filament. During deposition, the Ni(111) surface was held at 300 K. The AES ratios of Fe (600 eV)/Ni (849 eV) and Cu (922 eV) /Ni (718 eV) were used to determine the coverage of Fe and Cu on Ni(111), respectively.

#### **4.2.3 TPD and HREELS Experiments**

Propanal (Sigma-Aldrich, 97+%) and 1-propanol (Sigma-Aldrich, 99.7+%) were purified using freeze-pump-thaw cycles. All other gases were of research grade purity (99.99%) and introduced into the UHV chamber without further purification. The

purity of all chemicals was checked using mass spectrometry. The samples were heated at a linear rate of 3 K/s and doses are reported in langmuirs ( $1 L = 1 \times 10^{-6}$  Torr s) and uncorrected for ion gauge sensitivity.

A primary beam energy of 6 eV was used for all HREEL spectra. Angles of incidence and reflection were 60° with respect to the surface normal. All spectra were normalized by the elastic peak intensity and scaled by a multiplication factor as shown in figures.

## 4.3 Results

#### 4.3.1 Characterization of Fe/Ni and Cu/Ni Bimetallic Surfaces

For each bimetallic surface, the AES peak-to-peak heights were monitored and plotted in Figure 4.1 (a) and (b) as a function of deposition time for Fe and Cu on Ni(111), respectively. The distinct breakpoints in the intensity of both the substrate and the overlayer in each surface provided an approximate deposition time for 1 ML and indicated that the growth of Fe or Cu on Ni(111) followed a layer-by-layer growth mechanism. The AES ratio of Fe (600 eV)/Ni (849 eV) or Cu (922 eV) /Ni (718 eV) at the breakpoint was similar to that expected by the formation of 1 ML Fe or Cu on Ni. This layer-by-layer growth was consistent with the previous growth study of Fe ultrathin films on Ni(111) by LEED and STM<sup>57</sup> and that of thin Cu on Ni(111) at room temperature.<sup>58</sup> It has been reported that both Fe and Cu grow almost layer-by-layer on Ni(111) for the first few monolayers and then continue to grow in a three-dimensional growth mode.<sup>57,58</sup> The deposition temperature of 300 K was low enough for the metals to form an alloy for the Cu/Ni bimetallic surface.<sup>59</sup>



Figure 4.1 AES measurements following the deposition of (a) Fe and (b) Cu on Ni(111) at 300 K as a function of deposition time.

# 4.3.2 Reaction Pathways of Propanal on Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111)

# 4.3.2.1 Propanal DFT Calculations

The binding energies of propanal and propionyl on Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111) are summarized in Table 4.1, along with the corresponding optimized C–O and O–M bond distances. The optimized geometry of propanal on Ni(111) and Ni-based bimetallic surfaces is shown in Figure 4.2. The binding energy of 1-propanol on Ni(111) is –23.6 kJ mol<sup>-1</sup>, which is close to the value of –28.9 kJ mol<sup>-1</sup> reported in a previous study.<sup>60</sup> The binding energy trend for propanal is ML Fe/Ni(111) > Ni(111) > ML Cu/Ni(111). Propanal adsorbs on Ni(111) and ML Fe/Ni(111) in an  $\eta^2$  configuration, where both C and O atoms of the carbonyl group interact with the surface, whereas the adsorption on ML Cu/Ni(111) occurs via an  $\eta^1$  configuration, in which propanal is bound through the carbonyl O atom. This prediction is consistent with the

previous furfural adsorption study on the PdCu bimetallic surface where the addition of Cu favors the formation of  $\eta^1$  over  $\eta^2$  configuration.<sup>61</sup> The addition of Fe to Ni, on the other hand, further stabilizes the formation of the  $\eta^2$  configuration and the interaction of the carbonyl group with the surface, in agreement with the previous study.<sup>14</sup> It is also well known that aldehydes prefer the  $\eta^2$  configuration on Group VIII metal surfaces.<sup>62,63</sup> The bond length of the C–O for propanal adsorbed on all surfaces becomes longer than that in the gas phase (1.21 Å), with ML Fe/Ni(111) showing the largest increase of 0.12 Å. Such an increase in the C–O bond length is expected for the strong interaction in an  $\eta^2$ -(C,O) configuration. Removal of the hydrogen through C–H bond cleavage from propanal results in the formation of propionyl (CH<sub>3</sub>CH<sub>2</sub>C=O–) species. This species binds to all three surfaces much more strongly than propanal and shows a similar binding energy trend.



Figure 4.2 Top and side views of adsorption geometry of propanal on Ni(111), Fe/Ni(111) and Cu/Ni(111). (Ni, aqua; Fe, yellow; Cu, purple; C, black; O, red; H, white).

	Propanal (CH <sub>3</sub> CH <sub>2</sub> CHO)			 Propionyl (CH <sub>3</sub> CH <sub>2</sub> C=O–)		
surfaces	BE	С–О	O–M	 BE	C–O	O–M
	(kJ mol-1)	(Å)	(Å)	(kJ mol-1)	(Å)	(Å)
Ni(111)	-23.6	1.26	2.04	-181.8	1.28	1.95
ML Fe/Ni(111)	-116.6	1.33	1.94	-267.8	1.31	1.99
ML Cu/Ni(111)	-7.9	1.24	2.14	-66.6	1.26	2.03

Table 4.1Binding energies of propanal and propionyl on different surfaces

## 4.3.2.2 Propanal TPD

TPD experiments were performed to study the reaction pathways of oxygenates on Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111) surfaces. Propanal was dosed at the exposure of 4 L, corresponding to the saturation of the chemisorbed layer. The TPD spectra of desorbing gas phase species,  $H_2$  (m/e = 2), CO (m/e = 28), propanal (m/e = 58) and  $C_2H_4$  (m/e = 27), are shown in Figure 3 a, b, c and d, respectively. No other reaction products were detected. Smaller desorption peaks were observed at m/e = 16but were attributed to the cracking pattern of CO. Figure 4.3 a showed that H<sub>2</sub> desorbed at 350 K, with a high temperature shoulder at 420 K from Ni(111), at 395 K from ML Fe/Ni(111), and at 350 K from ML Cu/Ni(111). The observation of several weak and shoulder peaks for the desorption of  $H_2$  from ML Fe/Ni(111) and ML Cu/Ni(111) surfaces suggested multiple reaction pathways of propanal on the bimetallic surfaces. CO desorbed at 430 K, 406 K and 420 K on Ni(111), ML Fe/Ni(111), and ML Cu/Ni(111), respectively. Both  $H_2$  and CO TPD spectra for ML Cu/Ni(111) had smaller peak areas compared to the other two surfaces. At temperature below 200 K, TPD spectra of  $C_2H_4$  (m/e = 27) and propanal (m/e = 58) were similar since the former was one of the major cracking patterns of propanal. Higher desorption temperature peaks were assigned to  $C_2H_4$  which desorbed at 426 K from Ni(111) and at 406 K from ML Fe/Ni(111). Very little C<sub>2</sub>H<sub>4</sub> desorption was observed on ML Cu/Ni(111). The fragment

at m/e = 58, the most abundant in the cracking pattern of propanal, is shown in Figure 4.3 c.



Figure 4.3 TPD spectra of (a) m/e = 2 (H<sub>2</sub>), (b) 28 (CO and C<sub>2</sub>H<sub>4</sub>), (c) 58 (propanal) and (d) 27 (C<sub>2</sub>H<sub>4</sub>) following 4L propanal exposure on different surfaces.

The net reaction pathways of propanal on Ni(111), Fe/Ni(111) and Cu/Ni(111) can be summarized as follows.

aCH <sub>3</sub> CH <sub>2</sub> CHO →	aCO +	$3aH_2 +$	$2aC_{ad}$		(4.1)
<i>b</i> CH <sub>3</sub> CH <sub>2</sub> CHO →	<b>b</b> CO +	<b>b</b> C <sub>2</sub> H <sub>4</sub>	+	<b>b</b> H <sub>2</sub>	(4.2)
$cCH_3CH_2CHO \longrightarrow 3$	$BcC_{ad}$ +	$c O_{ad}$ +	$3cH_2$		(4.3)
CO yield= $a + b$	$\Rightarrow a = CC$	O yield - b			
C <sub>2</sub> H <sub>4</sub> yield= $b$	$\Rightarrow b = C_2$	H4 yield			

 $H_2$  yield = 3a + b + 3c =>  $c = (H_2 \text{ yield} - 3a - b)/3$ 

Reaction 4.1 represents the reforming pathway, producing CO,  $H_2$  and  $C_{ad}$ . Reaction 4.2 is the decarbonylation reaction, producing  $C_2H_4$  along with CO and  $H_2$ . Reaction 4.3 represents total decomposition, producing  $H_2$  as well as  $C_{ad}$  and  $O_{ad}$  which remain on the surface. The reforming activity, a, decarbonylation activity, b, and total decomposition activity, c, represent the stoichiometric amount of chemisorbed propanal(molecule per metal atom) undergoing each reaction pathway and were calculated based on CO, C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> yields. Quantification of propanal activity was performed by comparing the TPD peak areas of H<sub>2</sub> and CO products with those after saturation exposures of H<sub>2</sub> and CO on Ni(111). Detailed procedures to estimate the activity and the selectivity towards the reactions have been described previously.<sup>64,65,66</sup> Briefly, based on saturation coverages of H<sub>2</sub> and CO on Ni(111) previously reported in literature,  $\theta_{\rm H}^{\rm sat} = 1.0 \frac{\rm H_2}{\rm Ni}^{67}$  and  $\theta_{\rm CO}^{\rm sat} = 0.5 \frac{\rm CO}{\rm Ni}$ , <sup>68,69</sup> the yields of H<sub>2</sub> and CO from the TPD measurements were determined using equations 4.4 and 4.5 by comparing the TPD peak areas of H<sub>2</sub> and CO products with those after Saturation exposures of H<sub>2</sub> and CO products with those after saturation exposures of H<sub>2</sub> and CO products with those after Saturation the TPD measurements were determined using equations 4.4 and 4.5 by comparing the TPD peak areas of H<sub>2</sub> and CO products with those after saturation exposures of H<sub>2</sub> and CO products with those after saturation exposures of H<sub>2</sub> and CO products with those after saturation exposures of H<sub>2</sub> and CO products with those after saturation exposures of H<sub>2</sub> and CO products with those after saturation exposures of H<sub>2</sub> and CO on Ni(111).

$$H_2 \text{ yield} = \frac{\theta_H^{\text{sat}}}{P_H^{\text{sat}}} \cdot P_H^{\text{CH}_3 \text{CH}_2 \text{CHO}}$$
(4.4)

$$CO \text{ yield} = \frac{\theta_{CO}^{\text{sat}}}{P_{CO}^{\text{sat}}} \cdot P_{CO}^{\text{CH}_3 \text{CH}_2 \text{CHO}}$$
(4.5)

where  $P_{H}^{sat}$  and  $P_{H}^{CH_{3}CH_{2}CHO}$  are the TPD areas of the 2 amu peaks from saturation H<sub>2</sub> desorption and CH<sub>3</sub>CH<sub>2</sub>CHO reaction, respectively. Similarly,  $P_{CO}^{sat}$  and  $P_{CO}^{CH_{3}CH_{2}CHO}$  are the TPD areas of the 28 amu peaks from saturation CO desorption and CH<sub>3</sub>CH<sub>2</sub>CHO reaction, respectively. The C<sub>2</sub>H<sub>4</sub> yield was obtained from an experimentally determined sensitivity factor relative to CO by comparing the mass spectrometer sensitivity factors at equal concentrations of C<sub>2</sub>H<sub>4</sub> and CO as shown in equation 4.6.

$$C_{2}H_{4} \text{ yield} = \frac{\theta_{CO}^{\text{sat}}}{P_{CO}^{\text{sat}}} \cdot P_{C_{2}H_{4}}^{\text{CH}_{3}\text{CH}_{2}\text{CHO}} \cdot \frac{S_{28\,\text{amu}}^{\text{S}0}}{S_{27\,\text{amu}}^{\text{C}_{2}H_{4}}} \cdot \frac{S_{28\,\text{amu}}^{\text{S}0}}{S_{27\,\text{amu}}^{\text{C}_{2}H_{4}}}$$
(4.6)

where  $S_{27 \text{ amu}}^{C_2H_4}$  and  $S_{28 \text{ amu}}^{CO}$  are mass spectrometer sensitivities for 27 amu and 28 amu for ethylene and CO, respectively, and  $P_{C_2H_4}^{CH_3CH_2CHO}$  is the TPD area of 27 amu peak from

the CH<sub>3</sub>CH<sub>2</sub>CHO reaction. Blank experiments were also performed to determine the contributions from adsorbed H<sub>2</sub> and CO from the UHV background which were subtracted to obtain the final product yields. Table 4.2 summarized the activities and selectivities (in parenthesis) of propanal reactions on Ni(111), Fe/Ni(111) and Cu/Ni(111). The Ni(111) surface showed the highest reforming activity and total activity. The reforming activity of Fe/Ni(111) was significantly larger compared to Cu/Ni(111). The Fe/Ni(111) surface showed the highest decarbonylation activity to produce ethylene through C–O bond scission.

	Activity*				
Surfaces	decarbonylation	reforming	decomposition	Total	
Ni(111)	0.021 (7)	0.189 (66)	0.078 (27)	0.288	
Fe/Ni(111)	0.047 (27)	0.129 (73)	0.000	0.176	
Cu/Ni(111)	0.018 (15)	0.000	0.099 (85)	0.117	
	1				

<sup>\*</sup>molecule per metal atom

## 4.3.2.3 Propanal HREELS

HREELS experiments were performed to identify the surface reaction intermediates of propanal on different surfaces. The HREEL spectra of 4L propanal on Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111) surfaces at different annealing temperatures are shown in Figure4 a, b, and c, respectively. The vibrational features of propanal observed at 100 K on Ni(111) are assigned and summarized in Table 4.3:  $\delta$ (CCO), 669 cm<sup>-1</sup>;  $\rho$ (CH<sub>3</sub>), 987 cm<sup>-1</sup>;  $\nu_a$ (CCC), 1076 cm<sup>-1</sup>;  $\delta$ (CH<sub>3</sub>), 1400 cm<sup>-1</sup>;  $\delta$ (CH<sub>2</sub>), 1434 cm<sup>-1</sup>;  $\nu$ (CO), 1648 cm<sup>-1</sup>;  $\nu$ (CH<sub>2</sub>), 2881 cm<sup>-1</sup>;  $\nu$ (CH<sub>3</sub>), 2915 cm<sup>-1</sup>. The vibrational assignments were in agreement with the liquid phase spectrum<sup>70</sup> as well as the DFT frequency calculation of propanal on Ni(111). After heating to 135 K, the multilayers

desorbed and the intensities of all vibrational modes decreased. The  $\delta$ (CCO) mode at  $669 \text{ cm}^{-1}$  and the v(CO) mode at 1684 cm<sup>-1</sup> became broader, indicative of the beginning of the interaction between the skeletal aldehyde structure and the surface. At 200 K, the  $\delta$ (CCO) mode disappeared almost completely and the v(CO) mode became much broader and shifted to lower frequency, suggesting the interaction between the carbonyl C=O group and the Ni(111) surface to form an  $\eta^2(C,O)$ -propanal intermediate, in agreement with the DFT prediction. Further heating to 250 K resulted in the additional intensity reduction in the  $\delta$ (CCO) and v(CO) modes. The remaining modes in the 250 K spectrum were still characteristic of an  $\eta^2(C,O)$ -propanal intermediate. This was in agreement with the TPD result in Figure 3, which showed that the desorption of monolayer molecular propanal from Ni(111) occurred around 284 K. Upon heating the surface to 300 K, propanal began to decompose to form adsorbed CO, as evidenced by the presence of threefold bridge-bonded CO at 1731 cm<sup>-1</sup> and v(Ni-C) at 413 cm<sup>-1</sup>. The modes associated with propanal disappeared altogether at 300 K, and only modes associated with the bridge-bonded CO at 1731 cm<sup>-1</sup> and some surface hydrocarbon fragments remained. Further heating to 400 K resulted in CO and the C<sub>x</sub>H<sub>y</sub> fragments being the only adsorbed species.

HREELS studies of the thermal behavior of propanal on Fe/Ni(111) and Cu/Ni(111) bimetallic surfaces are shown in Figure 4 b and c, respectively. Propanal adsorbed molecularly on ML Fe/Ni(111) at 100 K with similar vibrational features observed on Ni(111), particularly as indicated by the presence of the v(CO) mode at 1684 cm<sup>-1</sup> and the  $\delta$ (CCO) mode at 663 cm<sup>-1</sup>. After heating to 135 K, the  $\delta$ (CCO) and the v(CO) modes became broader, suggesting that the C=O functional group started to interact with Fe/Ni(111) at 135 K. Further heating to 200 K resulted in a significant

attenuation of the  $\delta$ (CCO) and the *v*(CO) modes, followed by the appearance of the twofold bridge-bonded CO at 1840 cm<sup>-1</sup> and *v*(Ni-C) at 453 cm<sup>-1</sup>. The modes associated with the surface hydrocarbon fragments remained at 200 K. These changes indicated that propanal decarbonylation had occurred at 200 K on ML Fe/Ni(111), at a lower temperature than Ni(111), where decarbonylation was observed at 300 K. No noticeable changes in the spectra were observed upon heating the surface to 300 K, except an increase in the relative intensity of the CO stretching mode at 1840 cm<sup>-1</sup>. Upon further heating to 400 K, all modes associated with the surface hydrocarbon fragments and the CO stretching mode attenuated substantially, indicating that essentially all the hydrocarbon fragments decomposed to surface carbon and hydrogen atoms at 400 K on ML Fe/Ni(111).

Similar to Ni(111) and ML Fe/Ni(111), propanal adsorbed molecularly on ML Cu/Ni(111) at 100 K. Upon heating the surface to 135 K, several changes were observed: (1) the intensity of the  $\delta$ (CCO) mode at 656 cm<sup>-1</sup> and the  $\nu$ (CO) mode at 1691cm<sup>-1</sup> became broader and significantly reduced, (2) vibrational characteristics of propanal surface species attenuated, leaving only  $\delta$ (CH<sub>2</sub>) mode at 1441 cm<sup>-1</sup>, the  $\nu$ (CH<sub>3</sub>)and  $\nu$ (CH<sub>2</sub>) modes at 2922 and 2881cm<sup>-1</sup>, respectively, (3) a new vibrational mode appeared at 717 cm<sup>-1</sup>. These changes indicated that at 135 K, most of the surface species had decomposed to surface hydrocarbon fragments, suggesting that the decomposition of propanal started at a lower temperature on ML Cu/Ni(111), compared to Ni(111) and ML Fe/Ni(111). In addition, the relative intensities of the hydrocarbon fragments were lower at 135 K on ML Cu/Ni(111) compared to the other two surfaces, indicating that molecular desorption competed with decomposition. Further heating up to 400 K did not result in any significant changes in the spectra and no adsorbed CO

was observed. This was in agreement with the TPD results in Figure 3 which showed a significantly smaller CO desorption peak from ML Cu/Ni(111).

Overall, HREELS results from Figure 4.4 a, b and c indicated that propanal molecularly adsorbed on Ni(111), ML Fe/Ni(111), and ML Cu/Ni(111) at 100 K. The decarbonylation of propanal on Ni(111) proceeded through stable acyl species which remained on the surface at 250 K. On ML Fe/Ni(111), decarbonylation to produce CO occurred at a lower temperature of 200 K. No CO stretching mode was observed on ML Cu/Ni(111), where propanal decomposed to form surface hydrocarbon fragments as early as at 135 K.





Figure 4.4 HREEL spectra of 4 L propanal on (a) Ni(111), (b) ML Fe/Ni(111) and (c) ML Cu/Ni(111) surfaces.

Vibrational assignment of propanal in cm<sup>-1</sup> Table 4.3

Assignment type of mode	Infrared <sup>a</sup>	Calculated	Ni(111)
		on Ni(111) <sup>b</sup>	100 K <sup>c</sup>
v(CH <sub>3</sub> )	2966	2968	2915
$v(CH_2)$	2909	2764	2881
v(CO)	1730		1648
$\delta(\mathrm{CH}_2)$	1458	1452	1434
$\delta(\mathrm{CH}_3)$	1418	1384	1400
$v_{\rm a}$ (CCC)	1092, 1120	1059,1094	1076
$\rho(\mathrm{CH}_3)$	898	995	987
$\delta$ (CCO)	660	656	669

<sup>a</sup> Liquid phase, adapted from<sup>70</sup> <sup>b</sup> Calculated using DFT

<sup>c</sup> This work

In summary, DFT results from Table 4.1 predict that the binding energies of propanal and its reaction intermediate through the C–H bond scission, (CH<sub>3</sub>CH<sub>2</sub>C=O–), follow the trend of Fe/Ni(111) > Ni(111) > Cu/Ni(111). From TPD experiments, the monometallic Ni(111) surface shows the highest reforming activity and total activity. The addition of monolayer of oxophilic Fe to Ni(111) results in the largest C–O bond length increase for adsorbed propanal, compared to molecular propanal due to a strong interaction of the carbonyl group with the Fe/Ni(111) surface. In addition to the binding energy, the adsorption geometry of aldehydes significantly affects on the reaction intermediates and reaction pathways. Propanal binds on both Ni(111) and Fe/Ni(111) surfaces through an  $\eta^2$  configuration and on Cu/Ni(111) via an  $\eta^1$  configuration. Previously, a high hydrogenation selectivity to furfuryl alcohol from furfural on Cu is attributed to the preferred adsorption of furfural in the  $\eta^1$  configuration.<sup>71,72,73</sup> For propanal on Cu/Ni(111), although no hydrogenation products were observed in the TPD study, the Cu/Ni(111) surface shows a higher decomposition activity, producing gas-phase H<sub>2</sub>, C<sub>ad</sub> and O<sub>ad</sub> on the surface.

# 4.3.3 Reaction Pathways of 1-Propanol on Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111)

#### 4.3.3.1 1-Propanol DFT Calculations

The calculated binding energies of 1-propanol and propoxy on Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111) surfaces are shown in Table 4.4. Similar to propanal, the binding energy trend for 1-propanol is ML Fe/Ni(111) > Ni(111) > ML Cu/Ni(111). The optimized geometry of 1-propanol on all three surfaces shows that 1-propanol adsorbs on an atop binding site through the oxygen atom with the rest of the molecule being directed away from the surface. The C–O bond length of adsorbed 1-propanol on

all three surfaces becomes 0.04 Å longer than that in the gas phase. Removal of hydrogen through the O–H bond cleavage results in the formation of the n-propoxy (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O–) species. The binding energies of this species are significantly larger than those of 1-propanol on all surfaces while maintaining the trend of ML Fe/Ni(111) > Ni(111) > ML Cu/Ni(111).

1-Propanol(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH) Propoxy(CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O–) BE C-O O-M BE C-O Surfaces O-M  $(kJ mol^{-1})$  $(kJ mol^{-1})$ (Å) (Å) (Å) (Å) -32.4Ni(111) 1.46 2.18 -236.51.45 1.98 ML Fe/Ni(111) -105.61.46 2.17 -253.41.43 1.78 ML Cu/Ni(111) -21.11.46 2.18 -159.21.42 1.88

Table 4.4Binding energies of 1-propanol and propoxy on different surfaces

### 4.3.3.2 1-Propanol TPD

The TPD experiments were performed on Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111) surfaces exposed to an exposure of 4L 1-propanol. The desorbing gas phase species included H<sub>2</sub> (m/e = 2), CO (m/e = 28), and propanal (m/e = 58) as shown in Figure 4.5 a, b and d, respectively. Smaller desorption peaks were observed for C<sub>2</sub>H<sub>4</sub> (m/e = 27) but were attributed to the cracking pattern of 1-propanol since there were no corresponding desorption peaks at m/e = 26. No other reaction products were detected. The largest cracking pattern of 1-propanol (m/e = 31) monitored during TPD experiments in Figure 4.5 c showed that multilayer and monolayer desorption temperatures of 1-propanol from all three surfaces were approximately 160 K and 210 K, respectively. Hydrogen desorption occurred at 375 K from ML Fe/Ni(111) and

at 350 K and 420 K from ML Cu/Ni(111) as relatively weak broad peaks. CO desorbed at 433 K, 420 K and 415 K from Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111), respectively. The dehydrogenation product of 1-propanol was observed at m/e = 58 and was attributed to propanal on Ni(111). Propanal desorption at 325 K from Ni(111) was reaction limited as the desorption temperature of molecularly adsorbed propanal from Ni(111) was 284 K as shown earlier in Figure 4.3 c. No propanal desorption peak was observed from ML Fe/Ni(111) and a very small propanal desorption peak occurred at 320 K from ML Cu/Ni(111).



Figure 4.5 TPD spectra of (a) m/e = 2 (H<sub>2</sub>), (b) 28 (CO and C<sub>2</sub>H<sub>4</sub>), (c) 31 (1-propanol) and (d) 58 (propanal) following 4L 1-propanol exposure on different surfaces.

The net reaction pathways of 1-propanol on Ni(111), Fe/Ni(111) and Cu/Ni(111) can be summarized as follows.

$aCH_3CH_2CH_2OH \longrightarrow$	aCO + $4a$ H <sub>2</sub> +	$2aC_{ad}$	(4.7)
$b$ CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH $\longrightarrow$	<b>b</b> CH <sub>3</sub> CH <sub>2</sub> CHO +	<b>b</b> H <sub>2</sub>	(4.8)
$c$ CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH $\longrightarrow$	$3cC_{ad} + cO_{ad} +$	$4cH_2$	(4.9)
CO yield = aCH<sub>3</sub>CH<sub>2</sub>CHO yield = bH<sub>2</sub> yield =  $4a + b + 4c \Rightarrow c = (H_2 \text{ yield } -4a-b)/4$ 

Reaction 4.7 represents the reforming pathway, producing CO, H<sub>2</sub> and C<sub>ad</sub>. Reaction 4.8 is a dehydrogenation reaction, producing CH<sub>3</sub>CH<sub>2</sub>CHO along with H<sub>2</sub>. Reaction 4.9 represents total decomposition, producing C<sub>ad</sub>, O<sub>ad</sub> and H<sub>2</sub>. The reforming activity, *a*, dehydrogenation activity, *b*, and total decomposition activity, *c*, were calculated based on CO, CH<sub>3</sub>CH<sub>2</sub>CHO and H<sub>2</sub> yields. From quantification procedures similar to those outlined earlier for propanal, the calculated activities and selectivities (in paranthesis) of 1-propanol on Ni(111), Fe/Ni(111) and Cu/Ni(111) are summarized in Table 4.5. The Ni(111) surface showed the highest reforming activity and total activity. On Fe/Ni(111), the highest decomposition activity was observed and Cu/Ni(111) showed a reforming activity in between Ni(111) and Fe/Ni(111).

Table 4.5Reactivity of 1-propanol on different surfaces

	Activity <sup>*</sup>					
Surfaces	dehydrogenation	reforming	decomposition	Total		
Ni(111)	0.015 (5)	0.239 (82)	0.038 (13)	0.292		
Fe/Ni(111)	0.000	0.016 (9)	0.161 (91)	0.177		
Cu/Ni(111)	0.002 (4)	0.043 (96)	0.000	0.045		

### 4.3.3.3 1-Propanol HREELS

The HREEL spectra following the thermal behavior of 4L 1-propanol on Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111) surfaces are shown in Figure 4.6 a, b and c, respectively. The vibrational features observed at 100 K on Ni(111) are summarized in Table 4.6. In particular, the presence of v(OH) at 3179 cm<sup>-1</sup>,  $v_a$ (CCO) at 954 cm<sup>-1</sup>,

 $v_{\rm s}$ (CCO) at 873 cm<sup>-1</sup>, and  $\delta$ (CCO) at 467 cm<sup>-1</sup> suggested that 1-propanol adsorbed molecularly on Ni(111) at 100 K with the O-H bond intact. The vibrational assignments were generally in agreement with the gas phase spectrum<sup>74</sup> as well as the DFT frequency calculation of 1-propanol on Ni(111). It should be noted that the v(OH) mode was redshifted by approximately ~  $500 \text{ cm}^{-1}$  with respect to the 1-propanol gas phase mode at 3687 cm<sup>-1</sup>. Such a large red shift was also observed for 1-propanol adsorption on Rh(111),<sup>51</sup> where the v(OH) mode appeared at 3205 cm<sup>-1</sup>. After heating the surface to 160 K, the v(OH) mode disappeared, suggesting that 1-propanol reacted through an initial O-H bond cleavage. In addition, the onset of a feature at 1657 cm<sup>-1</sup> was assigned as the v(C=O) mode of an aldehyde surface species, representing a propanal-like intermediate. This was in agreement with TPD results which showed the desorption of propanal, the dehydrogenation product of 1-propanol, from Ni(111) at 325 K. It was observed that decarbonylation had occurred after heating the surface to 250 K, characterized by the appearance of the modes at 1731cm<sup>-1</sup> and 410 cm<sup>-1</sup> for threefold bridge-bonded CO and for v(Ni-C), respectively. No significant changes were observed upon heating the surface to 300 K. At 400 K, only modes associated with the surface hydrocarbon fragments remained.

The HREEL spectrum of 4L 1-propanol on ML Fe/Ni(111) at 100 K in Figure 4.6 b was similar to that of Ni(111) at the same temperature, indicating that 1-propanol adsorbed molecularly at 100 K on ML Fe/Ni(111) with the O–H bond intact. Upon heating to 160 K, most of the vibrational features of 1-propanol remained unperturbed, except for the disappearance of the v(OH) mode at 3132 cm<sup>-1</sup>, suggesting that the O–H scission occurred for at least a fraction of adsorbed 1-propanol. Heating to 200 K resulted in the molecular desorption of 1-propanol and the intensities of all modes

became weaker. Decarbonylation of 1-propanol to produce CO was observed after heating the surface to 250 K as indicated by the presence of the features of twofold bridge CO at 1826 cm<sup>-1</sup> and the metal-CO mode at 420 cm<sup>-1</sup>. Little change in spectra occurred till the surface was heated to 400 K, at which temperature only modes associated with the surface hydrocarbon fragments were observed.

The HREEL spectra following the thermal behavior of 4L 1-propanol on ML Cu/Ni(111) surface are shown in Figure 4.6 c. The presence of v(OH) at 3145 cm<sup>-1</sup>,  $v_a(CCO)$  at 954 cm<sup>-1</sup>,  $v_s(CCO)$  at 873 cm<sup>-1</sup>, and  $\delta(CCO)$  at 480 cm<sup>-1</sup> confirmed the molecular adsorption of 1-propanol on ML Cu/Ni(111) at 100 K, with the O–H bond intact. After heating the surface to 160 K, the v(OH) mode and most of the modes associated with 1-propanol disappeared, and only CH<sub>3</sub> and CH<sub>2</sub> vibrational modes remained on the surface. The HREEL spectra did not show evidence for propoxy as an intermediate, indicating that decomposition was rapid and the C–C bond scission occurred at an lower temperature on ML Cu/Ni(111), compared to Ni(111) and ML Fe/Ni(111). In addition, the relative intensities of the modes present at 160 K on ML Cu/Ni(111) were weaker than those on the other two surfaces, suggesting that molecular desorption also competed with decomposition. No noticeable changes were observed upon heating the surface up to 300 K. At 400 K, a very small CO stretching mode at 2036 cm<sup>-1</sup> appeared.

Overall, HREELS results from Figure 4.6 a, b and c indicated that 1-propanol molecularly adsorbed on Ni(111), ML Fe/Ni(111), and ML Cu/Ni(111) at 100 K. Upon heating to 160 K, the O–H bond cleavage occurred on Ni(111) and ML Fe/Ni(111) to form a propoxy intermediate. The reaction of 1-propanol on Ni(111) proceeded via a propanal-like intermediate. On ML Fe/Ni(111), decarbonylation to produce CO

occurred at 250 K. On ML Cu/Ni(111), decomposition occurred at a lower temperature to form CO and surface hydrocarbons.





Figure 4.6 HREEL spectra of 4 L 1-propanol on (a) Ni(111), (b) ML Fe/Ni(111) and (c) ML Cu/Ni(111) surfaces.

Assignment type of mode	Infrared <sup>a</sup>	Calculated	Ni(111) <sup>c</sup>
		on Ni(111) <sup>b</sup>	100 K
v(OH)	3687		3179
va(CH <sub>3</sub> )	2978	2974	2916
$v_{s}(CH_{3})$ , $v_{s}(CH_{2})$	2892	2948	2916
$\delta(\mathrm{CH}_2)$	1464	1467	1440
$\delta(\mathrm{CH}_3)$	1464,1393	1467, 1381	1360
$\rho(CH_2)$	1393	1381	1360
$\rho(CH_2)$	1300	1298	nr
$\delta$ (COH)	1218	1232	nr
$\rho(\mathrm{CH}_3)$	1063	1056	1049
$v_{a}(CCO)$	1047,971	1033, 938	954
$\rho(CH_3)$	898	873	873
$v_{\rm s}({\rm CCO})$	898	873	873
$\Upsilon(CH_2)$	685	742	744
$\delta(\text{CCC})$	463	461	467
$\delta(\text{CCO})$	463	461	467

Table 4.6Vibrational assignment of 1-propanol in cm<sup>-1</sup>

<sup>a</sup> Gas phase, adapted from<sup>74</sup>

<sup>b</sup> Calculated using DFT

<sup>c</sup> This work

nr = not resolved

In summary, the binding energies of 1-propanol and its reaction intermediate via the O–H bond scission, (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O–), show a similar trend of Fe/Ni(111) > Ni(111) > Cu/Ni(111), compared to propanal and its intermediate. Experimentally, a propanal-like intermediate is observed on Ni(111) before decomposition of propoxy to CO occurs. A similar decomposition mechanism has been reported for methanol on Pd(110)<sup>75</sup> and 1-propanol on Pd(111).<sup>51</sup> This result is also in agreement with the reported bond scission sequence (O–H >  $\alpha$ C–H >  $\alpha$ C–C) for propan-2-ol on Ni(111) via reflection absorption IR spectroscopy and TPD.<sup>55</sup> In contrast, the decomposition mechanism of 1-propanol on Fe/Ni(111) follows a well-known mechanism where the O–H bond is cleaved to form propoxy, followed by decomposition to form carbon

monoxide and surface hydrocarbons. 1-Propanol decomposes on Cu/Ni(111) without spectroscopic evidence for the propoxy intermediate.

## 4.4 Conclusions

Using DFT, TPD and HREELS, the reaction pathways of propanal and 1propanol are compared on Ni(111), Fe/Ni(111), and Cu/Ni(111) surfaces. Based on the results and the discussion presented above, important conclusions are summarized as below.

(1). The binding energies of propanal, propionyl, 1-propanol and propoxy follow the trend: Fe/Ni(111) > Ni(111) > Cu/Ni(111). Propanal adsorbs on both Ni(111) and Fe/Ni(111) surfaces through an  $\eta^2$  configuration and on Cu/Ni(111) via an  $\eta^1$ configuration. 1-Propanol adsorbs on an atop binding site of all surfaces through the oxygen atom with the rest of the molecule being directed away from the surface.

(2). Propanal adsorbs molecularly on all surfaces at 100 K. The Ni(111) surface shows the highest reforming activity and total activity. The highest decarbonylation activity to produce ethylene is observed for the Fe/Ni(111) surface. The Cu/Ni(111) surface shows the highest decomposition activity.

(3). 1-Propanol adsorbs molecularly on all three surfaces at 100 K with the O– H bond intact. The Ni(111) surface shows the highest reforming activity as well as total activity, and dehydrogenation to form propanal is also observed before decomposition to CO occurs. On Fe/Ni(111) and Cu/Ni(111), decomposition occurs to form CO and surface hydrocarbons, via a propoxy intermediate on the former.

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## Chapter 5

# UNDERSTANDING THE ROLE OF METAL-MODIFIED MO(110) BIMETALLIC SURFACES FOR C–O/C=O AND C–C BOND SCISSION IN C3 OXYGENATES

## 5.1 Introduction

The reactions of biomass-derived oxygenates on transition metal surfaces have been of particular interest in the field of heterogeneous catalysis as a promising way to produce value-added fuels and chemicals from renewable sources.<sup>77,78,79</sup> Catalytic transformation of oxygenates, particularly the most commonly studied alcohols and aldehydes,<sup>80</sup> includes but not limited to C–O/C=O bond scission to produce alkenes via deoxygenation, and C-C and C-H bond scission to produce syngas (CO and H<sub>2</sub>) via reforming reaction. Selective hydrodeoxygenation (HDO)/deoxygenation is one of the pivotal reactions to remove excess oxygen from bio-oils to produce transportation fuels without reducing the carbon chain length.<sup>81,82,83</sup> Reforming reaction, on the other hand, is an attractive alternative way to produce hydrogen from renewable biomass, instead of the current production method from natural gas and petroleum.<sup>8,6</sup> Typical HDO and reforming catalysts include precious metal based catalysts such as Pt<sup>84</sup> and Pd<sup>85,86</sup> but the use of such catalysts in large-scale biomass conversion is hindered by high costs and scarcity of precious metals.<sup>87</sup> Cost effective non-precious metal catalysts, however, suffer from low activity and rapid deactivation.<sup>47</sup> The search for enhanced catalytic activity of non-precious metal requires an understanding of reaction pathways of oxygenates on metal surfaces.

Recently, molybdenum carbide (Mo<sub>2</sub>C) and oxide (MoO<sub>3</sub>) have been reported to show high selectivity towards C–O/C=O bond scission without breaking the C–C bond.<sup>83, 88,89,13,90,91,92,93,94</sup> Since bimetallic catalysts often show superior catalytic performance and a unique ability to control the reaction chemistry of oxygenates,<sup>8,6</sup> in this work, we have investigated the reactivity and the reaction intermediates of C3 oxygenates, 1-propanol and propanal as probe molecules, on Mo(110) and metalmodified Mo(110) surfaces. Non-precious bimetallic surfaces, Ni/Mo(110) and Co/Mo(110), are selected since sulfided NiMo/Al<sub>2</sub>O<sub>3</sub> and CoMo/Al<sub>2</sub>O<sub>3</sub> have long been used as conventional petroleum hydrotreating catalysts.<sup>81,82,91</sup>

Characterization of the Ni/Mo(110) and Co/Mo(110) surfaces has been extensively studied via LEED, STM and AES; the investigations of the growth of Ni<sup>95,96,97,98</sup> and Co<sup>98,99,100,101</sup> overlayers on Mo(110) show that both Ni and Co grow layer-by-layer on Mo(110) at room temperature and form 3D islands upon annealing to > 600 K. Reactions of alcohols on clean Mo(110) and modified Mo(110) have been largely reported by Friend's group via surface science studies.<sup>102,103,104,105,106,107,108,109</sup> However, investigation of reactions of aldehydes on Mo(110) is limited; Mei *et al.* studied the reaction pathways of acetaldehyde via periodic spin-polarized density functional theory (DFT) simulations<sup>110</sup> and Queeney *et al.* reported the reaction of formaldehyde on Mo(110) using temperature programmed reaction and infrared reflectance absorbance spectroscopy.<sup>111</sup> To the best of our knowledge, there is no experimental UHV study of C3 aldehyde on pure Mo(110) and/or metal-modified Mo(110) surfaces.

Hence, in this study, we investigate the reaction of propanal on Mo(110), monolayer (ML) Ni/Mo(110) and ML Co/Mo(110) surfaces and compare with that of

1-propanol. We first identify the DFT binding energy trends of propanal and 1-propanol on Mo(110) and metal-modified Mo(110) surfaces. Using temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS), reaction products and intermediates are identified and possible reaction pathways are proposed. Briefly summarizing our results, the bond scission of C–C, C–O/C=O and C– H can be controlled via bimetallic surfaces. While Mo(110) is active for breaking both C=O and C–O bonds in propanal and 1-propanol to produce propene, metal-modified bimetallic surfaces show higher reforming activity and produce other C–C and C–H bond scission products. Our results demonstrate the feasibility of controlling reaction pathways of small oxygenates which can be extended for more complex biomassderived oxygenate platform molecules.

### 5.2 Theoretical and Experimental Methods

#### 5.2.1 DFT Calculations

All theoretical calculations were performed with the Vienna *Ab initio* Simulation Package (VASP).<sup>112,113,114</sup> Calculation procedures have been described in details previously.<sup>76</sup> Briefly, the PW91 functional within the generalized gradient approximation (GGA) was used to approximate the exchange-correlation energy. The energy cutoff was 396 eV. The model surfaces in all cases consisted of a periodic  $3 \times 3$ unit cell with four layers of metal atoms at (110) configuration separated by six equivalent layers of vacuum. The Ni/Mo(110) and Co/Mo(110) surfaces were modified by replacing all Mo atoms from the top layer with Ni or Co adatoms which occupied the epitaxial positions. The bottom two layers of the slab were fixed while the top two layers and the adsorbate were allowed to relax to reach the lowest energy configuration. Spin-polarization was corrected accordingly.

Propanal and propionyl were adsorbed via both  $\eta^1$  (through the O lone pair) and  $\eta^2$  (through both C and O atoms of the carbonyl groups) configurations on the atop sites of adjacent metal atoms. As the most representative one, the optimized geometry of propanal and 1-propanol on Mo(110) is shown in Figure 5.1 a and b, respectively. Propanal adsorbs on all surfaces in an  $\eta^2$  configuration, where both C and O atoms of the carbonyl group interact with the surface. This is in agreement with previous report that acetaldehyde adsorbs on Mo(110) via an  $\eta^2$  configuration.<sup>110</sup> 1-Propanol adsorbs on an atop binding site of all surfaces through the oxygen atom with the rest of the molecule being directed away from the surface. Binding energies were calculated using the equation:

## $BE_{ads/slab} = E_{ads/slab} - E_{slab} - E_{gas}$

where  $E_{ads/slab}$  is the total energy of the slab with adsorbates,  $E_{slab}$  is the energy of the slab, and  $E_{gas}$  is the energy of the adsorbates in the gas phase. For all calculations, 1/9 ML coverage was used.



Figure 5.1 Top and side views of adsorption geometry of (a) propanal and (b)1propanol on Mo(110). (Mo, cyan; C, grey; O, red; H, white).

## 5.2.2 Experimental

The experiments were performed in two ultrahigh vacuum (UHV) chambers, which have been described previously,<sup>76</sup> with a base pressure of  $1 \times 10^{-10}$  Torr. The Mo single-crystal sample is a (110) oriented, 1.50 mm thick disk (99.99%) that has a diameter of 12.00 mm. The crystal was spot welded directly to two tantalum posts which served as contacts for heating and cooling. The surface was cleaned by repeated cycles of Ne<sup>+</sup> sputtering at 300 K, followed by annealing at 1100 K. To remove carbon left on the surface, O<sub>2</sub> treatment at 1000 K was performed and the surface was then annealed

at 1100 K. This cleaning procedure was repeated until Auger electron spectroscopy (AES) measurements confirmed the absence of C or O on the surface. Bimetallic surfaces were then prepared using previously reported procedures.<sup>76</sup> Briefly, *3d* metals (Ni, Co) were deposited using physical vapor deposition (PVD). The evaporative PVD doser consisted of a tungsten filament with a high purity Ni or Co wire (99.9999+% from Alfa Aesar) wrapped around it, mounted within a tantalum enclosure. During deposition, the Mo(110) surface was held at 300 K. The AES ratios of Ni (849 eV)/Mo (190 eV) and Co (777 eV)/Mo(190 eV) were used to determine the Ni and Co monolayer coverages on Mo(110), respectively.

Propanal (Sigma-Aldrich, 97+%) and 1-propanol (Sigma-Aldrich, 99.7+%) were purified via successive freeze-pump-thaw cycles. The purity of all chemicals was checked using mass spectrometry. The surfaces were heated at a linear rate of 3 K/s from 110 K to 800 K and doses are reported in langmuirs ( $1 L = 1 \times 10-6$  Torr s) and uncorrected for ion gauge sensitivity. All HREELS measurements were performed with a primary beam energy of 6 eV and with the angles of incidence and reflection at 60° with respect to the surface normal.

## 5.3 Results

## 5.3.1 Adsorbate Binding Energy

The binding energies of propanal, propionyl ( $CH_3CH_2C=O^*$ ) from the removal of hydrogen through the C–H bond, 1-propanol and 1-propoxy( $CH_3CH_2CH_2O^*$ ) obtained after the O–H bond scission on monometallic Mo(110) and metal-modified Mo(110) are summarized in Table 5.1. Their corresponding optimized C–O bond lengths are shown in Table 5.2. Overall, the binding energy trend for all adsorbates is

Mo(110) > Co/Mo(110) > Ni/Mo(110). While in general the C–O bond length of the carbonyl group cannot be directly correlated with the binding strength, the DFT results in Tables 5.1 and 5.2 show that the C–O bond length trend is consistent with the binding energy trend for the  $\eta^2$  configuration. For example, the clean Mo(110) surface shows the strongest binding energy and the largest C–O bond distance of the adsorbed  $\eta^2(C,O)$ propanal, suggesting that the strong interaction between the carbonyl group and the Mo(110) surface weakens the C=O bond and likely makes its scission more facile. This correlation between the C-O bond lengthening and the C-O bond scission is in agreement with those previously reported in the literature for furfural studies on NiFe<sup>14</sup> catalysts and Mo<sub>2</sub>C<sup>13</sup> surfaces. Deposition of monolayers of Ni and Co on Mo(110) lowers the binding energies of the four adsorbates, suggesting potentially different reaction pathways from the pure Mo(110). As demonstrated in many studies,<sup>5</sup> bimetallic surfaces often show binding energies and reaction pathways that are different from the parent metals. For instance, previous DFT study of hydrogen and ethylene on Pd/Mo(110)<sup>115</sup> reported that the deposition of monolayer Pd reduces the binding energies compared to clean Mo(110). Since Ni and Pd are from the same group 10 metals, it could be expected that the binding energy trend of Ni/Mo(110) and Pd/Mo(110), as compared to Mo(110), should be similar.

	Propanal		Prop	oionyl	1-Propanol	1-Propoxy
	(CH <sub>3</sub> Cl	H <sub>2</sub> CHO)	(CH <sub>3</sub> CH	$H_2C=O^*)$	(CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH)	$(CH_3CH_2CH_2O^*)$
Configuration	$\eta^1$	$\eta^2$	$\eta^1$	$\eta^2$	$\eta^1$	$\eta^1$
Mo(110)	-29.8	-32.6	-61.1	-72.4	-14.4	-72.5
ML Ni/Mo(110)	-10.1	-15.2	-46.2	-50.1	-10.8	-53.4
ML Co/Mo(110)	-12.9	-23.6	-54.0	-59.7	-11.9	-58.9

## Table 5.1Binding energies of adsorbates on different surfaces

 Table 5.2
 Optimized C–O bond lengths of adsorbates on different surfaces

	Pro (CH <sub>3</sub> C	panal H2CHO)	Prop (CH <sub>3</sub> CH	ionyl I <sub>2</sub> C=O*)	1-Propanol (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH)	1-Propoxy (CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> O*)
Configuration	η1	η2	η1	η2	η1	η1
Mo(110)	1.42	1.42	1.33	1.36	1.46	1.41
ML Ni/Mo(110)	1.24	1.33	1.27	1.30	1.47	1.42
ML Co/Mo(110)	1.25	1.37	1.29	1.33	1.47	1.41

### 5.3.2 Reaction of Propanal on Mo(110), Ni/Mo(110) and Co/Mo(110)

TPD experiments were performed on Mo(110), Ni/Mo(110) and Co/Mo(110) surfaces after exposing to 2 L propanal; the 2 L exposure corresponded to a saturation of chemisorbed propanal. The desorbing gas phase species included H<sub>2</sub> (m/e = 2), CO (m/e = 28), ethylene (m/e = 27), and propene (m/e = 41), as shown in Figure 5.2 a, b, c and d, respectively. TPD spectra of propanal (m/e = 58) were also monitored and shown in Figure 5.2 e. No other reaction products were detected.



Figure 5.2 TPD spectra of (a) m/e = 2 (H<sub>2</sub>), (b) 28 (CO, C<sub>2</sub>H<sub>4</sub> and propanal), (c) 27 (C<sub>2</sub>H<sub>4</sub> and propanal), (d) 41 (propene) and (e) 58 (propanal) following 2L propanal exposure on different surfaces.

As shown in Figure 5.2 a, hydrogen desorbs from Mo(110) at two maxima at 400 K ( $\beta_1$ ) and 570 K ( $\beta_2$ ). The peak desorption temperatures from Ni/Mo(110) and Co/Mo(110) are lower at 332 and 370 K, respectively. The relatively small hydrogen desorption peak at 570 K on Co/Mo(110) is likely from the uncovered surface sites of

Mo(110). Previous TPD studies<sup>7</sup> reported that hydrogen, from the dissociation of  $H_2$ , desorbed from Mo(110) and ML Ni/Mo(110) at 370 K and 280 K, respectively. Such comparison indicates that hydrogen desorption from both Mo(110) and ML Ni/Mo(110) in the current study is reaction-limited from the decomposition of propanal.

For the Mo(110) surface, desorption peaks are observed at 268 K and 445 K for m/e = 27, 28 and 58, which are from the cracking patterns of propanal. This is confirmed based on the relative mass spectrometer sensitivities for these peaks and also by the similar desorption temperatures and peak shapes, as shown in the Supporting Information. Because the intensity of the m/e = 28 peak for Mo(110) is consistent with the propanal cracking pattern, CO is not produced from the reaction of propanal on Mo(110). The dominant desorption product is propene (m/e = 41) at 510 K, suggesting deoxygenation pathway of propanal on clean Mo(110).

On ML Ni/Mo(110), propanal cracking pattern contributions to m/e = 28 are convoluted as shoulder peaks at 268 and 445 K. The desorption peak at 322 K is due to the cracking pattern of ethylene since it is also observed at m/e = 27, while the peak at 368 K is from CO desorption. Overall, the reaction of propanal on Ni/Mo(110) produces both ethylene at 322 K and CO at 368 K. For the ML Co/Mo(110), CO desorbs at 368 K and appears to be the only carbon-containing product. Ethylene is not produced from this surface because the peaks at 268 and 445 K at m/e = 27 are from the cracking pattern of propanal. Propene is not observed from either Ni/Mo(110) or Co/Mo(110).

Possible reaction pathways of propanal on the three surfaces can then be summarized as follows: reforming reaction involves the C=O bond retention to produce CO and H<sub>2</sub> via C–H and C–C bond scission; decarbonylation reaction occurs via C–CO bond scission to produce ethylene and CO; deoxygenation reaction produces propene through selective C=O bond cleavage; and total decomposition occurs via complete dissociation of all bonds to produce adsorbed atomic carbon, oxygen and hydrogen.

$aCH_3CH_2CHO \longrightarrow aCO$	+	$3aH_2$	+	$2aC_{ad}$	Reforming (5.1)
$bCH_3CH_2CHO \longrightarrow bC_2H_4$	+	<i>b</i> CO	+	$bH_2$	Decarbonylation (5.2)
$cCH_3CH_2CHO \longrightarrow cC_3H_6$	+	$c\mathrm{O}_{\mathrm{ad}}$			Deoxygenation (5.3)
$dCH_3CH_2CHO \longrightarrow 3dCad$	+	$dO_{ad}$	+	$3dH_2$	Total Decomposition (5.4)
CO yield = $a + b$	=>	a = CO y	vield	- b	(5.5)
$C_2H_4$ yield = $b$	=>	$b = C_2 H_2$	4 yiel	d	(5.6)
$C_3H_6$ yield = $c$	=>	$c = C_3 H_6$	5 yiel	d	(5.7)
H <sub>2</sub> yield $= 3a + b + 3d$	=>	$d = (H_2 y)$	vield	-3a - b)	/3 (5.8)

As shown in the equations above, the activity of four reactions, *a*, *b*, *c*, and *d*, represents the stoichiometric amount of chemisorbed propanal (molecule per metal atom) undergoing each reaction pathway. Reactivity quantification is performed based on the procedures shown in the Supporting Information, modified from the previously described method<sup>76</sup> since there is no saturation coverage of CO on Mo(110) in literature and the results are summarized in Table 5.3.

			Activity <sup>*</sup>		
Surfaces	Reforming	Deoxygenation	Ethylene	Decomposition	Total
			Formation		
Mo(110)	0.000	0.032	0.000	0.023	0.055
		(58.2)		(41.8)	
NiMo(110)	0.011	0.000	0.064	0.044	0.119
	(9.2)		(53.7)	(37.1)	
CoMo(110)	0.064	0.000	0.000	0.036	0.099
	(64.2)			(35.8)	

Table 5.3Quantification of propanal on Mo(110), NiMo(110) and CoMo(110)surfaces. Selectivity percentages are shown in parentheses.

\* molecule per metal atom

TPD quantification suggests that a majority of propanal undergoes deoxygenation reaction and the rest undergoes total decomposition on Mo(110). The reaction pathways are significantly altered on Ni/Mo(110), which shows an increased activity for reforming and total decomposition. In addition, the ML Ni/Mo(110) surface shows a high activity for ethylene production. Reforming activity is even higher on Co/Mo(110), with the rest undergoing total decomposition. It should be pointed out that although the CO peak area is larger on Ni/Mo(110) than Co/Mo(110) in Figure 5.2 b, after taking mass balance into account as shown in equations 5.5, our quantification results indicate a higher reforming activity on Co/Mo(110). In other words, since CO is produced from both reforming and decarbonylation reactions, Ni/Mo(110) shows a smaller reforming activity due to its high ethylene yield. Overall, the highest activity is observed for deoxygenation via C=O bond scission on Mo(110), and reforming to produce syngas via C–C and C–H bond scission on Co/Mo(110).



Figure 5.3 HREEL spectra of 4 L propanal on (a) Mo(110), (b) ML Ni/Mo(110) and (c) ML Co/Mo(110).

HREELS experiments were performed to determine the surface reaction intermediates. The HREEL spectra of 4L propanal on Mo(110), ML Ni/Mo(110) and ML Co/Mo(110) surfaces at 110 K and 400 K are shown in Figure 5.3 a, b and c, respectively. The vibrational features of propanal observed at 110 K on Mo(110) are summarized in Table 5.4, along with the DFT-calculated frequencies of propanal on Mo(110). The main vibrational features are  $\delta$ (CCO), 650 cm<sup>-1</sup>;  $\rho$ (CH<sub>3</sub>), 973 cm<sup>-1</sup>;  $v_a$ (CCC), 1080 cm<sup>-1</sup>;  $\delta$ (CH<sub>3</sub>), 1389 cm<sup>-1</sup>;  $\delta$ (CH<sub>2</sub>), 1422 cm<sup>-1</sup>;  $\nu$ (CO), 1671 cm<sup>-1</sup>;  $\nu$ (CH<sub>2</sub>), 2900 cm<sup>-1</sup> and  $\nu$ (CH<sub>3</sub>), 2900 cm<sup>-1</sup>. The observation of these characteristic vibrational modes indicates that propanal adsorbs molecularly on Mo(110) at 110 K. After heating the surface to 400 K, the  $\nu$ (CO) mode at 1671 cm<sup>-1</sup> shift to a lower frequency, become broader and the intensity is reduced, suggesting that the carbonyl group interacts with the Mo(110) surface to form an  $\eta^2$ (C,O)–propanal surface intermediate, in agreement with the DFT prediction shown in Figure 1 a. In addition, the presence of most of the skeletal vibrational modes at 400 K suggests that the  $\eta^2$ (C,O)–propanal species is still stable at 400 K, consistent with the TPD result which shows that propene production occurs at temperature higher than 400 K.

Similar to Mo(110), propanal adsorbs molecularly on both ML Ni/Mo(110) and ML Co/Mo(110) at 110 K as indicated in Figure 5.3 b and c. Upon heating the surface to 400 K, however, the  $\delta$ (CCO) mode at around 650 cm<sup>-1</sup> and the  $v_a$ (CCC) mode at 1080 cm<sup>-1</sup> disappear from both surfaces, indicating that the skeletal structure of propanal disappears and the C–C bond scission has already occurred. In fact, the *v*(CO) mode also disappears and only modes associated with the surface hydrocarbon fragments remained. This is in agreement with the TPD results which show the desorption of C–C bond scission products between 200-400 K.

The major difference between the HREEL spectra of propanal on Mo(110) and bimetallic surfaces is that the decomposition of C–C–C and C=O on Mo(110) does not start until 400 K, whereas on the bimetallic surfaces the decomposition of C–C–C bond has already completed by 400 K.

Assignment	Infrared <sup>70</sup>	Calculated on	Mo(110)
type of mode		Mo(110) <sup>a</sup>	110 K <sup>b</sup>
<i>v</i> (CH <sub>3</sub> )	2966	2968	2900
$v(CH_2)$	2909	2968	2900
v(CO)	1730		1671
$\delta(CH_2)$	1458	1441	1422
$\delta(CH_3)$	1418	1355	1389
v <sub>a</sub> (CCC)	1092, 1120	1089	1080
$\rho(\mathrm{CH}_3)$	898	973	973
$\delta(CCO)$	660	592	650

Table 5.4Vibrational assignment of propanal in cm<sup>-1</sup>

<sup>a</sup> Calculated using DFT

<sup>b</sup> This work

#### 5.3.3 Reaction of 1-Propanol on Mo(110), Ni/Mo(110) and Co/Mo(110)

The reaction of 1-propanol on  $Mo(110)^{108}$  and  $Co/Mo(110)^{104}$  has been studied via TPD and HREELS by Friend *et al.* Since our focus is to compare the bond scission activity of Mo(110) and metal-modified Mo(110) surfaces, particularly the difference between C=O bond of aldehyde and C–O bond of alcohol under the same reaction conditions, here we will summarize our results for the reactions of 1-propanol for comparison. The TPD and HREELS results of 1-propanol on all three surfaces, vibrational assignments at 110 K and the DFT frequency calculations for 1-propanol on Mo(110) are provided in the Supporting Information.

The reaction activity of 1-propanol on all three surfaces is summarized in Table 5.5. In summary, 1-propanol on Mo(110) undergoes mainly deoxygenation via C–O bond scission, with trace amounts undergoing dehydrogenation to form propanal, propane and total decomposition to produce surface carbon, oxygen and hydrogen. The deoxygenation product, propene, is no longer present upon bimetallic modification. On both bimetallic surfaces, reforming activity is enhanced and, in addition to syngas, ethylene and propanal are also observed via decarbonylation and dehydrogenation. As shown in Supporting Information, HREEL results reveal that 1-propanol adsorbs molecularly at 110 K on all surfaces and decomposition occurs via the 1-propoxy surface intermediate from the O–H bond scission. The main difference between Mo(110) and bimetallic surfaces is that C–O bond scission on Mo(110) starts around 400 K whereas the C–C bond cleavage has begun at 200 K for a fraction of the 1-propoxide surface species on both Ni/Mo(110) and Co/Mo(110) and completed by 400 K. Similar to propanal, the highest selectivities are observed for deoxygenation, decarbonylation and reforming on Mo(110), ML Ni/Mo(110) and ML Co/Mo(110),

respectively. Overall, the results for 1-propanol on Mo(110) and Co/Mo(110) are consistent with those reported by Friend *et al.*<sup>108,104</sup>

Table 5.5Quantification of 1-propanol on Mo(110), NiMo(110) and CoMo(110)surfaces. Selectivity percentages are shown in parentheses.

					Activity*		
Surfaces	Re-	Deoxy-	Ethylene	Propanal	Propane	Decom-	Total
	forming	genation	Formation	Formation	Formation	position	
Mo(110)	0.000	0.054	0.000	0.010	0.004	0.014	0.082
		(65.9)		(12.2)	(4.9)	(17.1)	
NiMo(110)	0.027	0.000	0.039	0.007	0.000	0.002	0.075
	(36.0)		(52.0)	(9.3)		(2.7)	
CoMo(110)	0.086	0.000	0.055	0.003	0.000	0.010	0.154
	(55.8)		(35.7)	(1.9)		(6.5)	

\*molecule per metal atom

#### 5.4 Discussion

DFT results show that the binding energies of propanal and 1-propanol on Mo(110) can be reduced by the deposition of surface monolayers of Ni and Co, and that the binding energy trend is Mo(110) > Co/Mo(110) > Ni/Mo(110). HREELS results show that on all three surfaces both 1-propanol and propanal adsorb molecularly at 110 K. TPD results confirm that the major reaction pathways for propanal and 1-propanol are also similar: Mo(110) selectively cleaves the C–O/C=O bond to produce propene and shows the highest activity for deoxygenation; Ni/Mo(110) and Co/Mo(110) show an enhanced activity in the C–C and C–H bond scission.

The combination of TPD and HREELS measurements provide further insights into the reaction pathways of propanal and 1-propanol. For example, as compared in Figure 5.4, the observation of similar propene desorption temperatures and peak shapes suggests that Mo(110) is active for both C=O and C–O bond scission and that the decomposition pathways are similar for propanal and 1-propanol. This is consistent with the HREELS results which show the presence of similar type of surface intermediates that contain the C–C–C–O skeletal structure at 400 K on Mo(110),  $\eta^2$ (C,O)–propanal and 1-propoxide as shown in Figure 5.4. Compared to the bimetallic surfaces, Mo(110) is less active toward C–C bond cleavage, leading to the selective C=O/C–O scission at 400 K.



Figure 5.4 Comparison of propene (m/e = 41) formation and surface intermediates on Mo(110) at 400 K from propanal and 1-propanol.

In contrast, the deoxygenation reaction is no longer present on bimetallic surfaces, which favor the C–C and C–H bond scission to produce CO and H<sub>2</sub>. The absence of propene formation in TPD (Figure 5.2 and Figure 5.5) is consistent with the HREELS results (Figure 5.3 and Figure 5.6) of the dissociation of the C-C-C-O skeletal

structure. The primary difference between the two bimetallic surfaces is that for both oxygenates, reforming activity on Co/Mo(110) is larger than that on Ni/Mo(110). This is consistent with previous results which show that a bimetallic surface with higher oxygenate binding energies possess a higher reforming activity.<sup>65</sup>



Figure 5.5 TPD spectra of (a) m/e = 2 (H<sub>2</sub>), (b) 28 (CO and C<sub>2</sub>H<sub>4</sub>), (c) 27 (C<sub>2</sub>H<sub>4</sub>), (d) 41 (propene), (e) 43 (propane), (f) 58 (propanal) and (g) 31 (1-propanol) following 2L 1-propanol exposure on different surfaces.



Figure 5.6 HREEL spectra of 4 L1-propanol on (a) Mo(110), (b) ML Ni/Mo(110) and (c) ML Co/Mo(110)

The ML Ni/Mo(110) surface also shows the decarbonylation pathway to produce ethylene and CO. For propanal, ethylene is observed only on ML Ni/Mo(110) while for 1-propanol ethylene is observed on both Ni/Mo(110) and Co/Mo(110). It is worth noting, however, that Ni/Mo(110) consistently shows the highest selectivity toward ethylene production for both molecules.

Such differences in reactivity can be related to the binding strength. For example, propanal shows the largest binding energy on the Mo(110), indicating a strong interaction between the carbonyl group and the surface, stabilizing the adsorbed  $\eta^2(C,O)$ -propanal surface intermediate. In addition, the length of the C=O bond in adsorbed propanal on Mo(110) has also increased significantly, compared to that of molecular propanal, making C=O bond scission more facile. Previous studies of hydrodeoxygenation reaction of furfural on NiFe bimetallic catalyst<sup>14</sup> and Mo<sub>2</sub>C<sup>13</sup> also show a correlation between the C–O bond lengthening due to stronger binding of the carbonyl group on the catalytic surface and the C–O bond scission. On the other hand,

the lower binding energies of oxygenates on the bimetallic surfaces should be responsible for retaining the C–O/C=O bond, leading to an enhanced selectivity toward the C–C and C–H bond scission.

Furthermore, decomposition reaction studies of 2-propanol on Mo(110) and  $Co/Mo(110)^{102}$  have suggested that the difference in reaction pathways was attributed to the difference in the metal-oxygen bond strength. Calculations for oxygen binding energy (OBE) in Table 5.6 showed that the OBE follows a similar trend as those of propanal and 1-propanol where the binding energy is reduced upon bimetallic modifications, supporting the previous claim that a stronger Mo-O binding energy results in breaking the C–O bond due to a stronger thermodynamic driving force. It should be pointed out that under catalytic reaction conditions Mo and its bimetallic surfaces might be in the form of carbides and oxides.<sup>116</sup> The trend in the current study on metal-modified Mo(110) is similar to a previous study of a C2 oxygenate, ethylene glycol, on Mo<sub>2</sub>C and Ni-modified Mo<sub>2</sub>C surfaces.<sup>117</sup> For example, results from that study revealed that the unmodified Mo<sub>2</sub>C surface favored the C–O bond scission, while ML Ni/Mo<sub>2</sub>C was selective toward the C-C bond cleavage due to strong atomic carbon and oxygen binding energies on Mo<sub>2</sub>C.<sup>117</sup> The similar trends between the two studies suggest that results from the current paper should have relevance to Mo-based bimetallic catalysts.

Table 5.6	Ovvgen h	inding energy	at different hindin	r citec on all	three surfaces
1 abic 5.0	Oxygen 0.	muning chergy	at uniterent omung	s shes on an	unce surfaces

	Binding Energy (kJ/mol)				
Surface	Atop	Bridge	Four-Fold		
Mo(110)	-330.8	-399.0	-432.7		
ML Ni/Mo(110)	-293.2	-258.0	-279.3		
ML Co/Mo(110)	-369.7	-335.1	-335.0		

Our current studies not only confirm the importance of the binding strength of oxygen and C3 oxygenates in determining the reaction pathways but also shed light on the use of non-precious bimetallic surfaces to control bond scission. We hope our experimental observations would inspire further detailed DFT calculations to explain the role of Ni and Co admetals and how they change the electronic structures and subsequently the reaction network and activation barriers.

## 5.5 Conclusions

Results from this investigation provide insight into how the C–O/C=O, C–C, and C–H bond scission can be controlled by surface modification of Mo(110) with Ni and Co. The reactions of propanal and 1-propanol are compared on Mo(110), ML Ni/Mo(110) and ML Co/Mo(110) via DFT and parallel TPD and HREELS experiments. DFT results predict that the binding energies of 1-propanol, propanal, 1-propoxy and propionyl can be reduced by the modification of Mo(110) with Ni and Co admetals, which shows the trend Mo(110) > Co/Mo(110) > Ni/Mo(110). For both propanal and 1-propanol, a highly selective deoxygenation activity is observed on Mo(110) via the C=O/C=O bond cleavage to form propene although a small amount undergoes total decomposition. Deposition of a monolayer of Ni and Co on Mo(110) surface enhances the C–C and C–H bond scission. The Co/Mo(110) surface shows the highest selectivity for reforming to produce CO and H<sub>2</sub>, while the Ni/Mo(110) surface shows the highest selectivity for decarbonylation to produce ethylene and CO.

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#### Chapter 6

# REFORMING AND OXIDATIVE DEHYDROGENATION OF ETHANE WITH CO<sub>2</sub> AS A SOFT OXIDANT OVER BIMETALLIC CATALYSTS

#### 6.1 Introduction

Emission of CO<sub>2</sub>, a byproduct from many industrial processes and power plants, has increased with increasing energy demand and growing population.<sup>119</sup> While viable utilization and mitigation of CO<sub>2</sub> are critical for sustainable environmental impact, catalytically activating CO<sub>2</sub>, one of the most stable carbon-containing molecules, remains a challenge.<sup>18,120</sup> CO<sub>2</sub> can be activated to CO using hydrogen, via the reverse water gas shift (RWGS) reaction at relatively mild conditions.<sup>15</sup> To be carbon-efficient, the RWGS reaction requires inexpensive CO<sub>2</sub>-free hydrogen, instead of hydrogen produced from the steam reforming of methane (SRM) that produces CO<sub>2</sub> as a byproduct. Alternatively, CO<sub>2</sub> conversion to synthesis gas or syngas (CO and H<sub>2</sub>) can be achieved via dry reforming with the hydrogen-rich methane molecule (DRM). DRM is particularly attractive as it simultaneously transforms two abundant greenhouse gases into an important feedstock, syngas, which can be subsequently used in methanol and Fischer-Tropsch (FT) syntheses. Compared to SRM, DRM produces pure syngas without requiring the purification step and hence has lower operating cost.<sup>121,122</sup> However, DRM is highly endothermic and energy intensive due to high reaction temperatures, with most state-of-the-art DRM catalysts suffering from catalyst deactivation due to carbon deposition. For instance, Ni, the most common DRM catalyst, suffers serious deactivation.<sup>123</sup> Although the more expensive and scarce Ptgroup metals such as Pt, Pd, Rh and Ru are more resistant to carbon deposition,<sup>121,124</sup> their limited availability and high cost have hindered their applications in the DRM processes.

An alternative way to convert  $CO_2$  to syngas is to use ethane, the second-largest component of natural gas after methane.<sup>125</sup> Similar to methane reforming, dry reforming of ethane (DRE) (Equation 6.1) produces H<sub>2</sub>/CO via

$$C_{2}H_{6(g)} + 2CO_{2(g)} \rightarrow 4CO_{(g)} + 3H_{2(g)} \Delta H^{\circ}_{25} = 429 \text{ kJ/mol} \Delta G^{\circ}_{25} = 273 \text{ kJ/mol}$$
(6.1)

One significant advantage of DRE over DRM is that the former reaction reaches  $\Delta G < 0$  at a temperature that is approximately 100 K lower than that of the latter and thus potentially reducing the operating cost and catalyst deactivation.<sup>18</sup> Other reactions of CO<sub>2</sub> and ethane include oxidative dehydrogenation of ethane with CO<sub>2</sub> (ODEC) (Equation 6.2), non-oxidative dehydrogenation (Equation 6.3), cracking to produce methane (Equation 6.4) and RWGS to form water (Equation 6.5):

$$\begin{split} C_{2}H_{6(g)} + CO_{2(g)} & -> C_{2}H_{4(g)} + CO_{(g)} + H_{2}O_{(l)} \Delta H^{o}{}_{25} = 134 \text{ kJ/mol } \Delta G^{o}{}_{25} = 121 \text{ kJ/mol } (6.2) \\ C_{2}H_{6(g)} & -> C_{2}H_{4(g)} + H_{2(g)} & \Delta H^{o}{}_{25} = 137 \text{ kJ/mol } \Delta G^{o}{}_{25} = 101 \text{ kJ/mol } (6.3) \\ C_{2}H_{6(g)} + 2CO_{2(g)} -> CH_{4(g)} + 3CO_{(g)} + H_{2}O_{(l)} \Delta H^{o}{}_{25} = 180 \text{ kJ/mol } \Delta G^{o}{}_{25} = 122 \text{ kJ/mol } (6.4) \\ CO_{2(g)} & + H_{2(g)} -> CO_{(g)} + H_{2}O_{(g)} & \Delta H^{o}{}_{25} = 41 \text{ kJ/mol } \Delta G^{o}{}_{25} = 28 \text{ kJ/mol } (6.5) \end{split}$$

The ODEC reaction is an attractive method to produce ethylene, one of the most important building blocks in chemical industry used in the production of a variety of basic and intermediate products.<sup>126,127</sup> The ODEC reaction, where CO<sub>2</sub> acts as a soft oxidant, has potential advantages compared to using oxygen as an oxidant or the current production of ethylene from the highly energy intensive steam cracking of naphtha or ethane. Specifically, ODEC employs CO<sub>2</sub>, which can remove coke formed on the catalysts via the reverse Boudouard reaction (CO<sub>2</sub> + C -> 2 CO), thereby increasing

conversion and maintaining the stability of the catalysts. In contract, oxidative dehydrogenation of ethane with oxygen leads to total oxidation to produce the undesired CO<sub>2</sub> byproduct and hence results in low ethylene selectivity.<sup>128</sup>

While current research efforts focus heavily on DRM<sup>119,121,129</sup> and ODE with oxygen,<sup>130,131</sup> a comparative study of DRE and ODEC over bimetallic catalysts is still lacking. Some of the previously studied ODEC catalysts include Ga<sub>2</sub>O<sub>3</sub>- and Cr-based catalysts on various supports, mainly acidic supports such as SiO<sub>2</sub>.<sup>120,132</sup> Addition of Fe, Co and Mn has been shown to increase the activity of transition metal oxides.<sup>132,133,134</sup> Besides supported transition metal oxides, supported metal carbide, Mo<sub>2</sub>C/SiO<sub>2</sub>, has also been studied for ODEC.<sup>135</sup> Despite the initial high activity, these catalysts suffer from low stability.<sup>127,136</sup>

The primary objective of the current study is to identify low-cost and stable catalysts for both DRE and ODEC, using precious and non-precious bimetallic catalysts supported on CeO<sub>2</sub>. Specifically, the catalytic performance of CoPt/CeO<sub>2</sub>, previously reported as a selective catalyst for CO<sub>2</sub> activation by hydrogen,<sup>15</sup> is evaluated against its respective monometallic catalysts, Pt/CeO<sub>2</sub> and Co/CeO<sub>2</sub>, for the reaction of CO<sub>2</sub> and ethane. In order to replace Pt, several non-precious bimetallic catalysts, CoMo/CeO<sub>2</sub>, NiMo/CeO<sub>2</sub> and FeNi/CeO<sub>2</sub>, are selected for parallel catalytic performance evaluation. Reducible CeO<sub>2</sub> oxide, known for its ability to promote active metal dispersion and to shift easily between reduced and oxidized states which help accommodate CO<sub>2</sub> dissociation,<sup>137</sup> is used as the oxide support in this work. Our results indicate that CoPt/CeO<sub>2</sub> and NiMo/CeO<sub>2</sub> are active catalysts for DRE pathway to produce syngas, while FeNi/CeO<sub>2</sub> shows promising selectivity for the ODEC pathway to produce

ethylene. The experimental results are supported by DFT calculations of energetics for the DRE and ODEC pathways over CoPt and FeNi surfaces, respectively.

### 6.2 Materials and Methods

### 6.2.1 Catalyst Preparation

Monometallic (Pt, Co, Mo, Ni, and Fe) and bimetallic catalysts were synthesized by incipient wetness impregnation over as-is commercially obtained CeO<sub>2</sub> (35–45 m<sup>2</sup>/g, cubic, Sigma–Aldrich) supports, as described previously.<sup>15</sup> Precursor solutions were prepared by dissolving Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (Alfa Aesar), Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Alfa Aesar), H<sub>24</sub>Mo<sub>7</sub>N<sub>6</sub>O<sub>24</sub>.4H<sub>2</sub>O (Alfa Aesar), Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (Alfa Aesar) and Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O (Alfa Aesar). The catalysts were then dried at 353 K for 2–3 h and calcined at 563 K for 2 h. For all bimetallic catalysts, a co-impregnation synthesis procedure was used to maximize the number of bimetallic bond formation.<sup>138</sup> Metal loading amounts (atomic ratio of 1:3 for Pt:Co, Mo:Ni, Mo:Co, Ni:Fe) were selected to be consistent with the previous studies from our research group.<sup>15</sup>

### 6.2.2 Catalyst Characterization

#### 6.2.2.1 Pulse CO Chemisorption

Using an AMI-300ip (Altamira), pulse CO chemisorption was performed to compare the number of active sites in each supported catalyst. Approximately 200 mg of catalyst was added into a U-shaped quartz tube and dried at 393 K for 30 min, under helium with a constant flow rate of 50 ml/min. The reduction was performed with a heating rate of 10 K/min from 323 K to 723 K and held at 723 K for 45 min, using a mixture of 10%  $H_2$  in Ar (30 ml/min). Before pulse CO chemisorption experiments, the

reduced catalyst was purged in He (50 ml/min) at 723 K for 20 min for degassing and then cooled down to 313 K. A thermal conductivity detector (TCD) was used to analyze the amount of CO flowing out of the reactor. Pulses of 10% CO in He (loop 590  $\mu$ l) were injected onto a He stream (50 ml/min) until the peak area became constant. The amount of CO adsorbed by each catalyst provides a means to calculate the turnover frequency (TOF) and quantitatively compare the activity between each supported catalyst.

## 6.2.2.2 Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) was carried out in the same AMI-300ip (Altamira) instrument equipped with a thermal conductivity detector (TCD). Approximately 200 mg of catalyst was added into a U-shaped quartz tube and pretreated at 393 K for 30 mins in a He flow (30 ml/min) and then cooled to 323 K. The flow was then switched to a mixture of 10% H<sub>2</sub> in Ar with a constant flow rate of 30 ml/min and the TPR measurements were performed with a heating rate of 10 K/min to 723 K. The amount of hydrogen consumed as a function of reduction temperature was continuously monitored and recorded by TCD, which can be used to compare the reducibility of active metals in supported catalysts and to examine the alloy formation of the bimetallic catalysts.

#### 6.2.2.3 Flow Reactor Studies

Reactions of  $CO_2$  and ethane were performed in a <sup>1</sup>/<sub>4</sub> inch quartz reactor under atmospheric pressure. Approximately 100 mg of catalysts, sieved to 16-20 mesh, were used for steady-state experiments. Catalysts were reduced at 723 K for 1 h with a feed ratio of unity for H<sub>2</sub> and He (20 mL/min each). With the constant total flow rate at 40 mL/min, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and He as a diluent were introduced at 1:1:2 ratio, respectively, into the reactor. The catalysts were heated to 873 K and kept at this temperature for 12 h for steady-state measurements. Gas products were analyzed on-line using a gas chromatography (GC), equipped with a flame ionization detector (FID) and thermal conductivity detector (TCD). Control experiments were performed using a blank quartz reactor with and without the CeO<sub>2</sub> support at 873 K. Both cases show little activity, indicating that the gas-phase reaction, quartz sand and the support will not strongly affect the reaction.

For catalysts which show a selective dehydrogenation activity, the amount of  $H_2$  produced were below the detection limits of GC and therefore to be consistent, conversion and selectivity were defined as

$$Conversion = \frac{moles_{reactant}^{inlet} - moles_{reactant}^{outlet}}{moles_{reactant}^{inlet}} \times 100 \%$$

$$Selectivity_{i} = \frac{moles of \ carbon - containing \ product_{i}}{Sum \ of \ carbon - containing \ products} \times 100 \%$$

## 6.2.3 Density Functional Theory (DFT) Calculations

Density functional theory  $(DFT)^{139,140}$  calculations were performed using the Vienna *Ab-Initio* Simulation Package (VASP) code.<sup>114,112</sup> A plane wave cut-off energy of 400 eV and  $3 \times 3 \times 1$  Monkhorst-Pack<sup>39</sup> grid were used for total energy calculations. The interactions between the electrons and nuclei were treated with all electron like projector augmented wave (PAW) potentials with the generalized gradient approximation (GGA)<sup>141,142</sup> using PW91 functionals.<sup>143</sup> Ionic positions were optimized until Hellman-Feynman force on each ion was smaller than 0.02 eV/Å.
The Pt-terminated CoPt(111) surface was modeled using a four layer 3×3 surface slab. The Pt(111) surface was modified by replacing subsurface (2<sup>nd</sup> layer) Pt atoms with the Co atoms to model Pt-terminated CoPt(111) surface.<sup>6</sup> The mixed CoPt(111) and FeNi(111) surfaces were modeled using a four layer 4×4 surface slab. The Pt(111) surface was modified by replacing half of the Pt atoms in the top two layers with Co atoms to model a mixed CoPt(111) surface.<sup>6</sup> Similarly, the Ni(111) surface was modified by replacing half of the Ni atoms in the top two layers with Fe atoms to model a mixed CoPt(111) surface.<sup>6</sup> Similarly, the Ni(111) surface was modified by replacing half of the Ni atoms in the top two layers with Fe atoms to model a mixed FeNi(111) surface to mimic the slab configuration for the previously reported FeNi-supported catalysts.<sup>144</sup> A vacuum layer of ~14 Å thick was added in the slab cell along the direction perpendicular to the surface in order to minimize the artificial interactions between the surface and its periodic images. During geometry optimization, atoms in the top two layers were allowed to relax while the atoms in the bottom two layers were fixed. The binding energy of an adsorbate is calculated as

$$BE_{adsorbate} = E_{slab/adsorbate} - E_{slab} - E_{adsorbate}$$

where  $E_{slab/adsorbate}$ ,  $E_{slab}$  and  $E_{adsorbate}$  are the total energies of slab with adsorbate, clean slab and adsorbate species in gas phase, respectively.

## 6.3 **Results and Discussions**

## 6.3.1 Thermodynamic Analysis



Figure 6.1 Thermodynamic analysis of dry reforming of methane (green) and ethane (red) and oxidative dehydrogenation of ethane with CO<sub>2</sub> (blue) using the HSC Chemistry 8 software.

A thermodynamic analysis to investigate the effect of temperature on the Gibbs free energy ( $\Delta$ G) for DRM, DRE and ODEC from 298–1273 K is performed using the HSC Chemistry 8 software. As shown in Figure 6.1, temperature affects  $\Delta$ G significantly: while all of the above reactions are highly endothermic at low temperature (298 K) due to the stable nature of the reactants, an increase in temperature to ~ 1173 K results in thermodynamically favorable for all three reactions. It should be pointed out that the temperature at which  $\Delta$ G becomes zero varies significantly among the three reactions: the reaction temperature for DRE is lower by about 100 K and 200 K, compared to DRM and ODEC, respectively. This is in agreement with previous thermodynamic calculations by Xiaoding *et al.*<sup>18</sup> Lower reaction temperature for DRE means less energy required and possibly reduced catalyst deactivation problems which are typically associated with coking and sintering resulted from high reaction temperatures. At sufficiently high temperatures, both DRE and ODEC occur simultaneously and hence it is important to identify catalysts which kinetically control the selectivity toward each reaction.



Figure 6.2 Thermodynamic equilibrium plots for  $CO_2 + C_2H_6$  reaction at 1 atm from 373 - 1273 K and at inlet feed ratio of  $CO_2$ :  $C_2H_6 = 1$  with products (a) CO,  $H_2$  and  $H_2O$  only (b) CO,  $H_2$ ,  $H_2O$  and  $C_2H_4$ . The plots were created by using Gibbs free energy minimization algorithm on HSC Chemistry 8 software.

Although industrial processes rarely operate at equilibrium, it has been shown that a variety of reforming catalysts can achieve compositions close to equilibrium.<sup>119,145</sup> Hence, equilibrium plots provide insights for thermodynamic limitations and the effects of variables such as temperature and pressure.<sup>145</sup> Noureldin *et al.*<sup>145</sup> established thermodynamic trends for syngas production from the reforming of natural gas using thermodynamic equilibrium modeling in order to maximize hydrogen generation and economic benefits. Parkhare *et al.*<sup>146</sup> studied the equilibrium compositions for the DRE

process using the HSC Chemistry 7.1 software to identify the effect of reaction temperature. In this study, Gibbs free energy minimization simulation from the HSC Chemistry 8 software is used to generate thermodynamic equilibrium plots for the reactions of  $CO_2$  and ethane at an equimolar ratio. Figure 6.2a shows the equilibrium concentrations of the  $CO_2$  + ethane reaction with products CO, H<sub>2</sub> and H<sub>2</sub>O from 373 – 1273 K at 1 atm. The analysis indicates that the temperature affects equilibrium compositions significantly, particularly those of H<sub>2</sub> and CO. The ratio of H<sub>2</sub> to CO, an important variable for syngas generation, progressively increases starting at 473 K and reaches 0.75 at 853 K, as expected from the reaction stoichiometry. The H<sub>2</sub>/CO ratio then remains constant at 0.75 till 1273 K. Furthermore at 853 K, the ethane/CO<sub>2</sub> ratio approaches 0.5, consistent with the stoichiometric coefficients for DRE.

When simultaneous oxidative dehydrogenation reaction is considered, however, a different equilibrium composition is observed in Figure 6.2b after 823 K, where the production of ethylene begins. The ratio of  $H_2$  to CO increases and eventually approaches unity at 1273 K, consistent with stoichiometry for ODEC. Figure 6.2b also shows a higher ethane conversion at high temperature. Based on Figures 6.1, 2a and 2b, a reaction temperature of 873 K is selected to investigate the catalytic activity of supported bimetallic catalysts in a flow reactor at steady-state.

## 6.3.2 Catalyst Selection and Characterization

CoPt/CeO<sub>2</sub> has previously been identified as an active and selective catalyst for the catalytic reduction of CO<sub>2</sub> by hydrogen.<sup>15</sup> Compared to other bimetallic catalysts such as NiPt/CeO<sub>2</sub> and NiPd/CeO<sub>2</sub>, CoPt/CeO<sub>2</sub> produces the highest amount of the desirable product CO, instead of fully reducing CO<sub>2</sub> into CH<sub>4</sub>.<sup>15</sup> The combination of a reducible CeO<sub>2</sub> support with the active and selective CoPt bimetallic catalysts makes CoPt/CeO<sub>2</sub> a promising candidate for the reaction of CO<sub>2</sub> with ethane. However, in order to overcome the dependence for expensive and scarce precious metals, several nonprecious metal bimetallic catalysts are selected for this study. Particularly, the activities of CoMo/CeO<sub>2</sub> catalyst, which replaces Pt with Mo, as well as NiMo/CeO<sub>2</sub>, which employs Ni, the most common reforming transition metal, are investigated and compared with that of CoPt/CeO<sub>2</sub>. Furthermore, since Fe is known to enhance the catalytic activity of Cr-supported catalysts in ODEC,<sup>133</sup> FeNi/CeO<sub>2</sub> is also studied in this work.

#### 6.3.2.1 CO Uptake and Chemisorption

In order to obtain a quantitative comparison of the number of active sites on different catalysts via the amount of adsorbed CO, pulse CO chemisorption was performed. As shown in Table 6.1, the CO uptake values show the following trends: (1)  $CoPt/CeO_2 > Pt/CeO_2 > Co/CeO_2$ , (2)  $Co/CeO_2 > Mo/CeO_2 > CoMo/CeO_2$ , (3)  $NiMo/CeO_2 > Ni/CeO_2 > Mo/CeO_2$ , and (4)  $FeNi/CeO_2 > Fe/CeO_2 > Ni/CeO_2$ . In general, all bimetallic catalysts, except  $CoMo/CeO_2$ , have higher CO uptake values than those of the respective monometallic catalysts.

#### **6.3.2.2** Temperature Programmed Reduction (TPR)

The reducibility of active metals in supported catalysts is investigated using temperature programmed reduction (TPR) and the comparison of each bimetallic catalyst with respective monometallic catalysts is shown in Figures 6.3a, 3b, 3c and 3d for CoPt/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub>, NiMo/CeO<sub>2</sub> and FeNi/CeO<sub>2</sub>, respectively. Generally, the TPR profiles of bimetallic catalysts are different from those of monometallic catalysts, suggesting that the formation of bimetallic bonds affects the reduction kinetics. Figure

6.3a shows that the reduction peaks of CoPt/ CeO<sub>2</sub> shift to lower temperatures, compared to those of monometallic catalysts, indicating an increase in reducibility. However, the TPR profiles of CoMo/CeO<sub>2</sub> and NiMo/CeO<sub>2</sub> show a different trend. While the reduction peaks of both Co- and Ni-modified molybdenum bimetallic catalysts have higher reduction temperatures, compared to those of either Co or Ni alone, the bimetallic catalysts show lower reduction peak temperatures compared to the parent Mo/CeO<sub>2</sub> catalyst. This suggests that by modifying Mo with either Co or Ni, the reducibility of Mo is enhanced. In the case of FeNi/CeO<sub>2</sub>, while the bimetallic catalysts shows a very similar TPR profile as Fe/CeO<sub>2</sub> with similar reduction temperatures, FeNi/CeO<sub>2</sub> clearly has a higher peak area, compared to the parent catalysts, suggesting an increased reducibility. Overall, results in Figure 6.3 show a general increase in reducibility of active metals upon bimetallic formation.



Figure 6.3 TPR profiles for comparison of bimetallic catalysts with respective monometallic catalysts (a) CoPt/CeO<sub>2</sub>, Pt/CeO<sub>2</sub>, Co/CeO<sub>2</sub>, (b) CoMo/CeO<sub>2</sub>, Mo/CeO<sub>2</sub>, Co/CeO<sub>2</sub>, (c) NiMo/CeO<sub>2</sub>, Mo/CeO<sub>2</sub>, Ni/CeO<sub>2</sub>, and (d) FeNi/CeO<sub>2</sub>, Fe/CeO<sub>2</sub>, Ni/CeO<sub>2</sub>.

## 6.3.3 Catalytic Evaluation

## 6.3.3.1 Comparison of Bimetallic Catalysts

Table 6.1. summarizes the activity and selectivity of CoPt/CeO<sub>2</sub>, NiMo/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub>, FeNi/CeO<sub>2</sub> and the corresponding monometallic catalysts at 873 K. Figures 6.4a, and 6.4b show the conversion (%), and selectivity (%), respectively. Concentrations of carbon-containing products as a function of time on stream are shown in Figures 6.5 and 6.6 for bimetallic and monometallic catalysts, respectively.

Table 6.1Summary of flow reactor results for CO2 + Ethane reaction (10 mL/mineach) at 873 K diluted in 20 mL/min He. Values of conversion and selectivity calculatedby averaging data points between 500 – 700 min on stream

Catalyst <sup>*</sup>	Chemisorption	Conversion		TOF (min <sup>-1</sup> )		Selectivity for		
	(µmol CO/g)	(%)				Carbo	n-conta	ining
						Produ	cts	
		CO <sub>2</sub>	$C_2H_6$	$CO_2$	$C_2H_6$	CO	$CH_4$	$C_2H_4$
CoPt/CeO <sub>2</sub>	33.6	44.7	24.0	18.5	9.9	98.7	0.6	0.7
CoMo/CeO <sub>2</sub>	7.9	14.0	7.0	24.7	12.3	98.0	0.1	1.9
NiMo/CeO <sub>2</sub>	18.0	37.3	19.5	28.9	15.1	99.5	0.1	0.4
FeNi/CeO <sub>2</sub>	28.9	10.8	9.1	5.2	4.4	68.7	0.3	31.0
Pt/CeO <sub>2</sub>	23.2	18.2	8.8	10.9	5.3	97.0	0.4	2.6
Co/CeO <sub>2</sub>	10.2	19.4	4.7	26.6	6.5	99.3	0.1	0.6
Mo/CeO <sub>2</sub>	9.5	5.7	5.1	8.3	7.4	74.0	1.0	25.0
Ni/CeO <sub>2</sub>	12.0	20.5	13.3	23.8	15.4	93.7	0.2	6.1
Fe/CeO <sub>2</sub>	17.2	12.0	11.1	9.7	9.0	76.0	1.2	22.8

\*For bimetallic catalysts, the metal loading corresponds to a Co/Pt (Co/Mo, Ni/Mo or Fe/Ni) atomic ratio of 3 to 1. The metal loadings in monometallic catalysts are 1.7 wt%, 0.5 wt%, 0.8 wt%, 0.5 wt% and 0.5 wt% for Pt/CeO<sub>2</sub>, Co/CeO<sub>2</sub>, Mo/CeO<sub>2</sub>, Ni/CeO<sub>2</sub>, and Fe/CeO<sub>2</sub>, respectively.

As summarized in Table 6.1 and shown in Figure 6.4a, among the bimetallic catalysts, on the basis of the mass of the catalysts, CoPt/CeO<sub>2</sub> shows the highest conversions for CO<sub>2</sub> and ethane, 44.7 and 24.0%, respectively, – approximately over

two-fold higher than those in the monometallic catalysts. Upon replacing Pt with Mo, however, the conversions are reduced as much as three times, suggesting that CoMo/CeO<sub>2</sub> is less active than CoPt/CeO<sub>2</sub>. However, when Ni, instead of Co, is alloyed with Mo, conversions of CO<sub>2</sub> and ethane are comparable to those of the CoPt/CeO<sub>2</sub> catalyst, with 37.3 and 19.5% for CO<sub>2</sub> and ethane conversions, respectively. This is a particularly promising result since NiMo/CeO<sub>2</sub> is a precious metal free catalyst which can potentially reduce the need for precious metal catalysts for DRE. Figure 6.4b reveals that all three bimetallic catalysts, CoPt/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub>, NiMo/CeO<sub>2</sub>, show high selectivity of over 98% for the reforming product CO via the C–C bond cleavage.

When Fe is alloyed with Ni, on the other hand, despite relatively low conversions, the formation of ethylene is observed. The selectivity for ethylene is 30% for FeNi/CeO<sub>2</sub>, suggesting that FeNi shows promising selectivity to the ODEC reaction via the C–H bond cleavage. For all bimetallic reforming catalysts, conversions of CO<sub>2</sub> and ethane are approximately 2:1 and for the dehydrogenation FeNi/CeO<sub>2</sub> catalyst, conversions are nearly 1:1, consistent with the reaction stoichiometric coefficients, discussed previously in equations (6.1) and (6.2), respectively.



Figure 6.4 (a) Conversions of CO<sub>2</sub> and ethane, and (b) selectivities of CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> for reactions of ethane and CO<sub>2</sub> (10 mL/min each) diluted in 20 mL/min He at 873 K for CoPt/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub>, NiMo/CeO<sub>2</sub>, FeNi/CeO<sub>2</sub> and their respective monometallic catalysts.

The TOF values shown in Table 6.1, however, suggest a different trend due to varying CO uptake values. Among bimetallic catalysts, the TOF trend of CO<sub>2</sub> shows that NiMo/CeO<sub>2</sub> > CoMo/CeO<sub>2</sub> > CoPt/CeO<sub>2</sub> > FeNi/CeO<sub>2</sub>, resulting from low CO uptake in molybdenum-based bimetallic catalysts.

## 6.3.3.2 Comparison of Bimetallic Catalysts with Corresponding Monometallic Catalysts

As shown in Table 6.1 and Figure 6.4a, the CoPt/CeO<sub>2</sub> catalyst shows the highest activity on the basis of mass, compared to its monometallic catalysts, Pt/CeO<sub>2</sub> and Co/CeO<sub>2</sub>. The TOF values in Table 6.1, in contrast, show that Co/CeO<sub>2</sub> has the highest TOF due to its low CO uptake. Selectivity at similar conversions, although not included, shows that all CoPt/CeO<sub>2</sub>, Pt/CeO<sub>2</sub> and Co/CeO<sub>2</sub> catalysts have over 97% selectivity for the reforming product CO, suggesting that all catalysts favor the reforming pathway via the C–C bond cleavage. The stability is significantly enhanced in the bimetallic

CoPt/CeO<sub>2</sub> catalyst as evident in Figures 6.5a, 6.6a, and 6.6b. In the case of the CoMo/CeO<sub>2</sub> bimetallic catalyst, both the activity and TOF show the same trend: Co/CeO<sub>2</sub> > CoMo/CeO<sub>2</sub> > Mo/CeO<sub>2</sub>. While both Co/CeO<sub>2</sub> and CoMo/CeO<sub>2</sub> lead to CO selectivity over 98%, Mo/CeO<sub>2</sub> shows approximately 25% for ethylene selectivity. This means that by modifying Mo with Co, the selectivity could be tuned from partially selective to dehydrogenation to highly selective toward the reforming pathway. In addition, the CoMo/CeO<sub>2</sub> catalyst has a higher stability compared to either monometallic catalyst.

For NiMo/CeO<sub>2</sub>, modification of Mo with Ni enhances the activity of the bimetallic catalyst compared to either parent metal catalyst. In addition to the activity, bimetallic formation also considerably improves the stability. As shown in Figure 6.6d, the deactivation of Ni/CeO<sub>2</sub> is significant, in agreement with previous reports.<sup>[121]</sup> In contrast, the stability is significantly improved in the NiMo/CeO<sub>2</sub> catalyst. Similar to CoMo/CeO<sub>2</sub>, NiMo/CeO<sub>2</sub> shows over 99% selectivity for the reforming pathway. This result suggests that a highly active and stable non-precious NiMo/CeO<sub>2</sub> catalyst can be used to replace the need for the precious metal CoPt/CeO<sub>2</sub> catalyst for the DRE reaction. When Ni/CeO<sub>2</sub> is modified to form FeNi/CeO<sub>2</sub>, the bimetallic catalyst shows a promising selectivity toward the ODEC pathway to form ethylene with selectivity up to 30%. In addition, FeNi/CeO<sub>2</sub> shows an increased stability compared to the corresponding monometallic catalysts.

A comparison of results in Figures 6.5 and 6.6 also reveals differences in the stability of monometallic and bimetallic catalysts. Generally, as shown in Figure 6.5 the stability of all bimetallic catalysts is enhanced compared to the corresponding monometallic catalysts in Figure 6.6.



Figure 6.5 Concentration of carbon-containing products for reactions of ethane and CO<sub>2</sub> (10 mL/min each) diluted in 20 mL/min He at 873 K for (a) CoPt/CeO<sub>2</sub>, (b) CoMo/CeO<sub>2</sub>, (c) NiMo/CeO<sub>2</sub> and (d) FeNi/CeO<sub>2</sub> plotted versus time on stream.



Figure 6.6 Concentration of carbon-containing products for reactions of ethane and CO<sub>2</sub> (10 mL/min each) diluted in 20 mL/min He at 873 K for (a) Pt/CeO<sub>2</sub>, (b) Co/CeO<sub>2</sub>, (c) Mo/CeO<sub>2</sub>, (d) Ni/CeO<sub>2</sub> and (e) Fe/CeO<sub>2</sub> plotted versus time on stream.

#### 6.3.4 Reaction Pathways via DFT Calculations

The CoPt and FeNi bimetallic systems are further investigated using DFT to gain more mechanistic insights for the DRE and ODEC pathways, respectively. As a simplified representation of the dominant plane of nanoparticles of CoPt and FeNi, model surfaces of CoPt(111) and FeNi(111) with the most thermodynamically stable facet are constructed. Based on previous studies, Pt-terminated CoPt(111),<sup>6</sup> mixed  $CoPt(111)^6$  and mixed FeNi(111)<sup>144</sup> surface are selected to investigate the energy profile during the reaction. The binding energies of potential reaction intermediates for C-C and C-H bond cleavage for the reaction of ethane and CO2 are calculated on the Ptterminated CoPt(111), mixed CoPt(111), and mixed FeNi(111) surfaces shown in Figures 6.7a, 6.7b, and 6.7c, respectively. In these calculations the surfaces are modified by oxygen atoms from the dissociation of  $CO_2$ . The results in Table 6.2 show that all intermediates bind more strongly on mixed CoPt(111) and FeNi(111) than on Ptterminated CoPt(111). In addition, the results show that the binding energy difference between Pt-terminated CoPt(111) and the mixed surfaces is more pronounced for species adsorbed via the oxygen atom than those via the carbon atom (Figure 6.8) mainly because of significantly enhanced O binding on the mixed surfaces.

Table 6.2 DFT calculated binding energies (in eV) of potential ethane dehydrogenation intermediates and atomic O on Pt-terminated CoPt(111) and mixed CoPt(111) and FeNi(111) surfaces.

Species	Pt-terminated CoPt(111)	Mixed CoPt(111)	Mixed FeNi(111)
Н	-2.40	-2.78	-2.87
Ο	-3.46	-5.25	-5.87
CO	-1.10	-1.69	-1.84
CH <sub>3</sub>	-1.68	-1.94	-2.19
CH <sub>2</sub> CH <sub>2</sub>	-0.37	-0.79	-0.94
CH <sub>2</sub> CH	-2.00	-2.79	-2.96
CH <sub>3</sub> CH <sub>2</sub>	-1.51	-1.75	-1.82
CH <sub>3</sub> CH <sub>2</sub> O	-1.43	-2.27	-3.17
CH <sub>3</sub> CHO	-0.24	-0.69	-0.65
CH <sub>3</sub> CO	-1.84	-2.57	-2.31



Figure 6.7 DFT optimized slabs models. Side (top) and top (bottom) views of (a) Ptterminated CoPt(111) and (b) mixed CoPt(111) and (c) mixed FeNi(111) surfaces. Light grey: Pt, blue: Co, aqua: Ni and brown: Fe, respectively.



Figure 6.8 DFT calculated energetically most favorable binding configurations. Side (top) and top (bottom) views of (a) H, (b) O, (c) CO, (d) CH<sub>3</sub>, (e) CH<sub>2</sub>CH<sub>2</sub>, (f) CH<sub>2</sub>CH, (g) CH<sub>3</sub>CH<sub>2</sub> (h) CH<sub>3</sub>CH<sub>2</sub>O, (i) CH<sub>3</sub>CHO, and (j) CH<sub>3</sub>CO on the Pt-terminated CoPt(111) surface. Light grey: Pt, blue: Co, dark grey: C, red: O and green: H, respectively.

The change in energy for the oxidative C–C and C–H bond cleavage of ethane is calculated on all three surfaces with two atomic oxygen preadsorbed on all surfaces. The energy profiles are shown in Figures 6.9a, 6.9b and 6.9c for the Pt-terminated CoPt(111) surface, the mixed CoPt(111) and the mixed FeNi(111) surfaces, respectively. Here the energy change is calculated for the reforming pathway via the C– C bond cleavage leading to products  $CH_3^*$ ,  $CO^*$  and  $H_2O(g)$ . For the oxidative dehydrogenation pathway, the energy change is calculated along a pathway via the C– H bond cleavage leading to products  $CH_2CH^*$  and  $H_2O(g)$ . For all surfaces, the atomic hydrogen is assumed to react with \*O on the surface to form  $H_2O(g)$ .



Figure 6.9 DFT calculated energy profile of reforming and oxidative dehydrogenation of ethane on (a) Pt-terminated CoPt(111), (b) mixed CoPt(111), and (c) mixed FeNi(111).

Figure 6.9a shows that on Pt-terminated CoPt(111), the C–C bond cleavage of ethane to form  $CH_3^*$ ,  $CO^*$  and  $H_2O$  (g) is exothermic, and energetically more favorable compared to the selective C–H bond scission to form  $CH_2CH_2^*$ . In particular, it is found that the oxidation of ethane to form  $CH_3CH_2O^*$  is energetically more favorable than the dehydrogenation of ethane to form  $CH_3CH_2^*$ . The  $CH_3CH_2O^*$  species subsequently undergoes two successive dehydrogenation reactions to form  $CH_3CO^*$ , which then undergoes C–C bond cleavage to form  $CH_3^*$  and  $CO^*$ . Thus, the DFT results suggest that the Pt-terminated CoPt(111) surface promotes the reforming pathway to form CO.

This is in agreement with the flow reactor experimental studies shown in Table 6.1. Interestingly, however, the DFT calculated energy profile on the mixed CoPt(111) surface in Figure 6.9b does not show similar trend to that on the Pt-terminated CoPt(111) surface, and the mixed surface is neither selective to C–C bond scission nor C–H bond scission. This result suggests that CoPt/CeO<sub>2</sub> could be Pt-terminated under reaction conditions or experiments performed in the current study.

In contrast to the Pt-terminated CoPt(111) surface, DFT calculations predict a different reaction scheme on the mixed FeNi(111) surface. On the mixed FeNi(111) surface, as shown in Figure 6.9c, the pathway for selective C–H bond cleavage (leading to product  $CH_2CH_2*$ ) is energetically more favorable than the pathway for C–C bond cleavage. Thus the FeNi(111) surface is predicted to preferentially dehydrogenate ethane to form  $CH_2CH_2$ . The DFT prediction supports the flow reactor data for the detection of ethylene as one of the major products over the FeNi/CeO<sub>2</sub> catalyst in Table 6.1.

#### 6.4 Conclusions

The catalytic performance of precious metal bimetallic catalyst, CoPt/CeO<sub>2</sub>, and non-precious metal bimetallic catalysts, CoMo/CeO<sub>2</sub>, NiMo/CeO<sub>2</sub>, and FeNi/CeO<sub>2</sub> is compared for the reaction of CO<sub>2</sub> and ethane. In general the catalytic stability is enhanced in all bimetallic catalysts over the corresponding monometallic catalysts. In terms of selectivity, CoPt/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub>, and NiMo/CeO<sub>2</sub> favor the reforming pathway to produce syngas via the C–C bond cleavage, while FeNi/CeO<sub>2</sub> shows promising selectivity to the oxidative dehydrogenation pathway to produce ethylene via the C–H bond cleavage. DFT calculated energy profiles on CoPt/CeO<sub>2</sub> and FeNi/CeO<sub>2</sub> confirm different reaction pathways, consistent with the experimental results.

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## Chapter 7

## DESIGNING NON-PRECIOUS METAL ELECTROCATALYST WITH HIGH ACTIVITY FOR HYDROGEN OXIDATION REACTION IN ALKALINE ELECTROLYTES

#### 7.1 Introduction

The alkaline nature of hydroxide exchange membranes enables the utilization of earth-abundant non-precious metal catalysts for electrolyzers,<sup>147</sup> solar hydrogen generators,<sup>148</sup> and fuel cells,<sup>149</sup> and this new generation of electrochemical devices can provide a safe, clean and sustainable hydrogen based energy system. Contrary to the hydrogen evolution/oxidation reaction (HER/HOR) in proton exchange membrane based electrolyzer and fuel cell systems, where the HER/HOR on Pt are fast with a negligible overpotential,<sup>150</sup> the HER/HOR reactions are much slower on Pt in alkaline electrolytes.<sup>21</sup> Such slow kinetics would significantly reduce the cell efficiency, and consequently require a higher loading of the Pt catalyst. It is therefore critical to investigate the HER/HOR in alkaline environment in order to obtain fundamental understanding and to develop more efficient electrocatalysts. It has been generally accepted that the HER activity in terms of exchange current density in acid correlates well with the chemisorption energy of hydrogen to the metallic surfaces by a volcano plot, revealing that an optimal hydrogen binding energy (not too strong and not too weak) would lead to the highest activity.<sup>3, 151</sup> Greeley et al.<sup>4, 152</sup> have demonstrated that the exchange current densities on Pd monolayer deposited on a series of substrates in acid follow the volcano relationship with HBE. The bi- or tri-metallic surface configuration modifies the HBE such that Pd/Pt and Pd/PtRu surfaces show one order of magnitude enhancement of the exchange current density over Pd in acid electrolyte.<sup>152</sup> Furthermore, recent findings<sup>153</sup> show that MoS<sub>2</sub> has higher HER exchange current density over Mo, ascribed to its weaker HBE.<sup>153b, 154</sup> Esposito *et al.*<sup>155</sup> have found that Pt monolayer on WC and Pt exhibit almost identical HER activity, attributed to their similar HBE values. These observations suggest that the HER activity can be tuned by modifying the hydrogen binding strength of the electrocatalysts, and therefore HBE can be used as a screening tool for catalyst design. However, it is unclear whether HBE can be used as a descriptor for the HER/HOR in alkaline solution, which should be answered first in order to develop more efficient electrocatalysts in alkaline medium.

Due to the fact that not many metals except Pt-group metals show appreciable HOR activity in alkaline electrolyte, HER was used as a probe reaction to examine the catalytic activity of a series of monometallic surfaces, and the relationship between the HER exchange current density and the HBE of the corresponding surfaces was investigated. The result shows that a volcano type of correlation also applies in alkaline electrolyte. This indicates that HBE can be used as a useful descriptor for the HER in base, similar to the case in acid, which suggests the possibility of tuning electrochemical activity by modifying the surface chemical properties.

Based on this volcano relationship, NiMo and CoNiMo electrocatalysts were prepared by electrodeposition and their HOR activity in 0.1 M KOH was studied using temperature controlled rotating disk electrode method. The electroplated NiMo and CoNiMo multi-metallic catalysts exhibit significantly enhanced HOR activity over electroplated Ni catalyst in KOH electrolyte (20 times). To qualitatively understand the HOR activity trend, density functional theory (DFT) calculations and parallel  $H_2$ temperature-programmed desorption ( $H_2$ -TPD) experiments were performed on structurally much simpler alloy systems that are more accessible to DFT calculations and TPD experiments. The results suggest that a weakened HBE is a significant contributing factor for the improved HOR on multi-metallic NiMo and CoNiMo catalysts.

#### 7.2 Theoretical and Experimental Method

#### 7.2.1 Density Functional Theory (DFT) Calculations

The HBE values were calculated using the Vienna *Ab initio* Simulation Package (VASP).<sup>113-114, 156</sup> The exchange-correlation energy was approximated using the PW91 functional within the generalized gradient approximation (GGA) with a basis set of plane waves up to an energy cutoff of 396 eV. In all cases, the model surface consisted of a periodic  $3\times3$  unit cell with four layers of metal atoms corresponding to the most closed-packed configurations separated by six equivalent layers of vacuum. The two bottom layers of the slab were fixed while the top two layers were allowed to relax to reach the lowest energy configuration. Spin-polarization was included for all surfaces. All calculations were performed on close-packed surfaces of single crystals, i.e., close-packed (111) facet of the fcc structure and the (110) facet of the bcc structures. The advantage of performing DFT calculations on single crystal surfaces is that the predicted trend can be verified experimentally using H<sub>2</sub>-TPD.

The Ni/Mo(110) surface was modified by replacing all Mo atoms from the top layer with Ni atoms. The Ni-Co-modified Mo(110) surface was prepared by replacing a third of Mo atoms from the top layer with Co atoms and the rest from the top layer

with Ni atoms as shown in Figure 7.1. While it is not uncommon to have surface intermixing or subsurface alloying in multi-metallic systems, the highly favorable surface segregation energy of Ni or CoNi on Mo suggests that pseudomorphic overlayer of Ni and Co on Mo(110) is a good representation of the surfaces measured experimentally. A  $3\times3\times1$  Monkhorst-Pack k-point mesh was used. Binding energy was calculated using equation:<sup>4</sup>

$$E_{atomic}^{H} = E_{H-slab} - E_{slab} - 0.5 \times E_{H2(g)}$$

where  $E_{atomic}^{H}$  is the binding energy of atomic hydrogen on the given slab,  $E_{H-slab}$  is the energy of the slab with 1/9 ML hydrogen adsorbed,  $E_{slab}$  is the energy of the slab in vacuum, and  $E_{H2(g)}$  is the energy of hydrogen in the gas phase. Different adsorption sites, such as atop, bridge, fcc, and hcp, were calculated, but only the value corresponding to the most stable binding site was included in Table 7.1.



Figure 7.1 Top and side views of adsorption geometry of hydrogen on CoNi/Mo(110) (Mo, pink; Ni, blue; Co, cyan; H, white).

#### 7.2.2 Hydrogen Temperature Programmed Desorption (H<sub>2</sub>-TPD)

The ultrahigh-vacuum (UHV) chamber used in this study is a two-level stainless steel chamber with a base pressure of  $1 \times 10-8$  Torr equipped with Auger electron spectroscopy (AES) for surface characterization and a quadrupole mass spectrometer (MS) for TPD experiment. The Mo single-crystal sample is a (110) oriented disk (99.99%) that has a thickness of 1.50 mm and a diameter of 12.00 mm. The crystal was spot welded directly to two tantalum posts which served as thermal contacts and electrical connections. Hydrogen, oxygen and neon were all of research grade purity (99.99%).

The Mo(110) surface was cleaned by repeated cycles of Ne+ sputtering at 300 K and annealing at 1100 K. Following the last sputter cycle, 1 Langmuir (1 L = 1x10-6 Torr s) of O2 at 1000 K was used to remove carbon left on the surface, followed by annealing at 1100 K This cleaning procedure was repeated until negligible C or O was detected by AES. The surface was then modified by depositing 3d metals (Ni, Co) using physical vapor deposition (PVD). The evaporative PVD doser consisted of a tungsten filament with a high purity Ni or Co wire (99.9999+% from Alfa Aesar) wrapped around it, mounted within a tantalum enclosure. During deposition, the Mo(110) surface was held at 600 K. The Ni (849 eV)/Mo (190 eV) AES ratios were used to determine the Ni monolayer coverage on Mo(110). The Ni-Co-modified Mo(110) surface was prepared by depositing ~ 1 ML of Ni, followed by ~ 0.5 ML of Co on Mo(110) held at 600 K.

## 7.3 Results and Discussion

The hydrogen binding energies (HBE) of monometallic surfaces and their corresponding most stable binding sites are summarized in Table 7.1. In order to explore the relationship between the HER activity and HBE, the HER exchange current densities

(from electrochemical measurements performed by Dr. Wenchao Sheng) are plotted as a function of calculated HBE values of these monometallic surfaces as shown in Figure 7.2. It is clear that Pt is still the best catalyst for the HER in alkaline showing the highest exchange current density, similar to that in the acidic medium.<sup>3, 151b</sup> W, Fe, Ni, Co and Pd are located on the left-branch of the volcano curve because they bind to hydrogen too strongly while the opposite is true for Cu, Ag and Au. As the HBE of a metal increases or decreases from that of Pt, its HER activity decreases by orders of magnitude. As pointed out by the Sabatier principle and many previous studies,<sup>3, 151</sup> neither too strong nor too weak binding would favor the overall reaction because strong or weak binding leads to either difficulty in removing the final product or poor adsorption of the reactant. This principle appears to apply in both basic and acidic electrolytes where Pt has the optimal HBE. This volcano curve strongly suggests that the HBE can be a useful descriptor for identifying HER electrocatalysts.

	$\Delta E_{\rm H}$	Н	log(i <sub>0</sub> (A/cm <sup>2</sup> me	roughn	Tafel Slopes of
	(eV)	adsorption	tal))	ess	the HER
		site		factor	(mV/dec)
Ag	0.25	FCC	$-7.3\pm0.3$	1.7	$-134 \pm 9$
Au	0.14	FCC	$-6.2\pm0.6$	2.2	$-168 \pm 9$
Cu	-0.20	FCC	$-5.8\pm0.2$	6.1	$-226 \pm 25$
Pt	-0.46	FCC	$-3.20\pm0.01$	1.6	$-113 \pm 1$
Pd	-0.62	FCC	-3.9	1.7	-210
Co	-0.51	FCC	$-5.5\pm0.4$	2.5	$-126 \pm 6$
Ni	-0.51	FCC	$-5.1\pm0.5$	1.9	$-135 \pm 32$
Fe*	-0.59	four-fold	$-4.9\pm0.4$	-	$-131 \pm 12$
		hollow			
W*	-0.80	two-fold	$-7.2\pm0.4$	-	$-90 \pm 7$
		bridge			

Table 7.1Calculated hydrogen binding energy on mono- and bi-metallic surfacesand measured exchange current densities, log(i0), roughness factors and Tafel slopes.



Figure 7.2: Exchange current densities, log(i<sub>0</sub>) on monometallic surfaces plotted as a function of the calculated HBE. All data are listed in Table 1. The dashed lines are to guide the eyes.

The HER in base proceeds in the following sequence of Volmer-Heyrovsky or Volmer-Tafel mechanisms: <sup>157</sup>

Volmer:  $H_2O + e^- + * \leftrightarrow H_{ad} + OH^-$ Heyrovsky:  $H_{ad} + H_2O + e^- \leftrightarrow H_2 + OH^- + *$ Tafel:  $2H_{ad} \leftrightarrow H_2 + 2^*$ 

where \* represents the hydrogen adsorption sites. Compared to the HER in acid, the reactant in base is water instead of hydronium ( $H_3O^+$ ). In the above elementary reaction steps, adsorbed hydrogen ( $H_{ad}$ ) appears to be the only reaction intermediate on the electrode surface, similar to the case in the acidic electrolyte. Consequently adsorption and removal of adsorbed H atoms become competitive processes. This competition does not seem to be affected by the presence of anions such as  $CIO_4-$ ,  $SO_4^{2-}$  and  $CI^-$  in acids or  $OH^-$  anions in base, although the absolute HBE values are mostly likely modified by

the surrounding anion species.<sup>158</sup> Therefore, an optimal HBE is still desired to maintain the balance between the adsorption and removal of the H intermediate in base.

To probe qualitatively if HBE plays an important role in multi-metallic CoNiMo catalyst, hydrogen binding energy (HBE) values were calculated using DFT on structurally simpler model surfaces such as Mo(110), ML Ni/Mo(110) and CoNiMo(110), and compared with those on Ni(111) and Pt(111). In addition, parallel H<sub>2</sub>-TPD measurements were also carried out to confirm the binding energy trend predicted by DFT. As shown in Table 7.3, DFT calculations show that Ni(111) and Mo(110) have notably higher HBEs than Pt(111), NiMo exhibits much lower HBE than Ni and Mo, and CoNiMo possesses an HBE value between those of NiMo and Pt.

	Mo (110)	Ni (111)	ML Ni/Mo (110)	CoNi/Mo (110)	Pt (111)
Binding Energy (eV)	-0.70	-0.51	-0.40	-0.43	-0.46
Binding Energy (kJ/mol)	-67.6	-49.5	-38.6	-41.6	-44.7
Binding Site	bridge	fcc	bridge	bridge	fcc
Bond Length (Å)	1.90	1.71	1.64	1.66	1.87
Bond Angle	44.8	42.5	38.4	37.7	39.0

Table 7.3Hydrogen binding energies from DFT calculations for the mostenergetically favorable binding site for each surface.

Figure 7.3 shows that the HBE trend calculated from DFT is consistent with the  $H_2$ -TPD measurements. Specifically, Ni(111) and Mo(110) exhibit higher  $H_2$  desorption temperatures, and therefore higher hydrogen binding energies, than Pt(111) (340 K for

Ni(111), 370 K for Mo(110), and 325 K for Pt(111)). Also consistent with the DFT trend, the  $H_2$  desorption temperature is decreased to 280 K when the Mo(110) surface is modified with one monolayer of Ni. Further modification of the NiMo bimetallic surface with Co leads to a  $H_2$  desorption temperature (300 K) between NiMo and Mo surfaces. It should be pointed out that Ni- and CoNi-modified Mo(110) surfaces show lower desorption temperatures than the clean Ni(111) surface, in agreement with the DFT trend.



Figure 7.3 TPD spectra of  $H_2$  desorption from various mono- and multi-metallic surfaces.

Rotating disk electrode method was employed to evaluate the HOR performance of the bimetallic and multi-metallic catalyst systems. As illustrated in Figure 7.4a, electroplated Ni exhibits little HOR activity, while NiMo shows significantly increased HOR activity. The activity of NiMo can be further enhanced with Co electroplated simultaneously. The HOR activity appears highly dependent on the atomic ratio between Co and Ni in the plating solution as shown in Figure 7.4b. The CoNiMo electroplated from the precursor solution containing Co, Ni and Mo with an atomic ratio of 0.12 : 5.10 : 1.00 showed the highest HOR activity. The HOR polarization curve of polycrystalline Pt disk is also presented in Figure 7.4a as a benchmark of HOR performance.



Figure 7.4 (a): Steady state polarization curves of the HOR/HER on electroplated Ni, NiMo, CoNiMo and polycrystalline Pt disk. The ratio by each curve refers to the atomic ratio between Co, Ni and Mo in the plating solution; (b): the HOR currents at 0.05 V vs. RHE as a function of the  $C_{Co}/(C_{Co}+C_{Ni})$  in the plating solution. The polarization curves were collected in H<sub>2</sub>-saturated 0.1 M KOH and with a rotating speed of 1600 rpm at room temperature.

The kinetic currents (ik) of the HOR on CoNiMo and Pt were calculated using the Koutecky-Levich equation<sup>159</sup>

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_D}$$

where i is the measured current and  $i_D$  is the diffusion limited current. The kinetic currents of the HOR/HER were subsequently fitted to the Butler-Volmer equation<sup>159</sup> to obtain exchange current

$$\mathbf{i}_{k} = \mathbf{i}_{0} \left( \mathbf{e}^{\frac{\alpha_{a}F}{RT}\eta} - \mathbf{e}^{\frac{-\alpha_{c}F}{RT}\eta} \right)$$

where i<sub>0</sub> is the exchange current,  $\alpha_a$  and  $\alpha_c$  are transfer coefficients for the HOR and HER, respectively, F is the Faraday's constant (96485 C/mol), R is the universal gas constant (8.314 J/mol/K), T is temperature, and  $\eta$  is the overpotential. The exchange current density, obtained through normalization of the total exchange current by the electrochemical surface area of CoNiMo and Pt at 293 K are listed in Table 7.4. The i<sub>0</sub> of HOR/HER on Pt is determined to be  $0.61\pm0.05$  mA/cm<sup>2</sup><sub>Pt</sub>, which is in excellent agreement with the previous study.<sup>21</sup> The i<sub>0</sub> of the HOR/HER on CoNiMo varies from  $0.007\pm0.001$  to  $0.015\pm0.002$  mA/cm<sup>2</sup><sub>Ni</sub>, depending on the fitting parameter ( $\alpha_a + \alpha_c$ ). Because Ni alone barely shows any HOR activity in the vicinity of the hydrogen reversible potential, it is not practical to extract the exchange current density of Ni at 0 V vs. RHE. Therefore, the kinetic current densities of Ni and CoNiMo at 0.05 V vs. RHE are calculated and listed in Table 7.4 for comparison. CoNiMo shows 20 times higher HOR activity than Ni at 0.05 V vs. RHE, suggesting a significant improvement due to the addition of Co and Mo elements. Thus, the HBE values appear to be critical in controlling the HOR activity for the catalysts used in the current study.

	i <sub>0</sub>	$i_{k,0.05V}$	Ea
	$(mA/cm^{2}_{metal})$	$(mA/cm^{2}_{metal})$	(kJ/mol)
Pt disk	$0.61 \pm 0.05$	1.44±0.13	29±1
	$0.015 \pm 0.002$		35±1
CoNiMo	$(\alpha_a + \alpha_c = 1)$	$0.044 \pm 0.005$	$(\alpha_a + \alpha_c = 1)$
COMINIO	$0.007 \pm 0.001$	$0.044\pm0.003$	36±1
	$(\alpha_a + \alpha_c = 2)$		$(\alpha_a + \alpha_c = 2)$
Ni	-	0.002	-

Table 7.4The HOR/HER exchange current densities and kinetic activities at 0.05V vs. RHE on Pt disk, CoNiMo and Ni at 293 K and activation energies.

#### 7.4 Conclusions

In summary, the correlation between the HER exchange current densities and the HBE values has been established in alkaline medium via a volcano plot, similar to that in acid, which suggests that the HER activity could be tailored by tuning the surface chemical properties such that an optimal HBE value can be obtained. This knowledge is extended to design and develop more efficient electrocatalysts for alkaline-based electrolyzers, solar hydrogen and fuel cell devices. Based on this volcano relationship, a highly active precious-metal-free Ni-based HOR electrocatalyst is synthesized and our results suggest that the specific HOR activity of CoNiMo is 20 times higher than Ni in alkaline medium. The remarkably enhanced activity is ascribed to the weakened hydrogen binding energy on CoNiMo. This innovative material can potentially mitigate the catalyst cost issue by providing a pathway to non-precious metal catalysts as viable replacement to Pt at the anode of alkaline or alkaline membrane fuel cells.

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## Chapter 8

## **CONCLUSIONS AND FUTURE PROSPECTS**

#### 8.1 Summary of Results

The objective of this thesis has been to design efficient non-precious bimetallic catalysts with specific functionality based on fundamental understanding of bonding and reactivity for heterogeneous catalysis and electrocatalysis. The three reactions addressed in this work share a common rational catalyst design – to identify more active, selective and stable precious-metal-free bimetallic catalysts. The use of non-precious metal catalysts can overcome the challenges associated with large-scale catalytic commercial applications of precious metal catalysts such as high cost and limited worldwide supply.<sup>6</sup>

## 8.1.1 Controlling Reaction Pathways of C3 Oxygenates on Non-precious Bimetallic Surfaces

This dissertation has demonstrated how the binding strengths and the adsorption geometry of C3 oxygenates, predicted by DFT, can be correlated with the reactivity and selectivity, experimentally measured by TPD and HREELS. The combination of theoretical and experimental techniques provides compelling insights into the reaction pathways of the C3 oxygenate probe molecules – propanal and 1-propanol – on non-precious Ni-based bimetallic surfaces, Ni(111), ML Fe/Ni(111) and ML Cu/Ni(111). Overall, the binding energy trends of propanal, 1-propanol, and their respective reaction intermediates – propionyl and propoxy – show that Fe/Ni(111) > Ni(111) > Cu/Ni(111).

It is also predicted from DFT that propanal binds on both Ni(111) and Fe/Ni(111) through an  $\eta^2$  configuration and on Cu/Ni(111) via an  $\eta^1$  configuration. TPD quantification shows that the unmodified Ni(111) surface has the highest reforming activity and total activity. By modifying Ni(111) with oxophilic Fe, the bimetallic ML Fe/Ni(111) surface shows the largest C–O bond lengthening for adsorbed propanal, resulting from a strong interaction of the carbonyl group with the surface. While the ML Fe/Ni(111) surface shows the highest decarbonylation activity to produce ethylene, the ML Cu/Ni(111) surface shows the highest decomposition activity. For 1-propanol, similar activity is observed for Ni(111), which shows the highest reforming activity and total activity via a propanal-like intermediate before the decomposition of propoxy to CO occurs. On Fe/Ni(111), decomposition leads to the formation of CO and surface hydrocarbons via a propoxy intermediate through the O–H bond cleavage while no spectroscopic evidence for propoxy intermediate is observed on Cu/Ni(111).

The study of reactions of propanal and 1-propanol has also been extended on Mo-based bimetallic surfaces. The binding energy trends of propanal and 1-propanol, as well as their corresponding reaction intermediates, show that Mo(110) > Co/Mo(110) > Ni/Mo(110). This suggests that the binding energy can be reduced upon metal modification of Mo(110) with Co and Ni. For propanal, a strong interaction between the carbonyl group and the Mo(110) surface makes C=O bond scission more facile, leading to a highly selective deoxygenation activity to produce propene. The deoxygenation pathway is no longer present on bimetallic surfaces, which favor the C–C and C–H bond scission to produce CO and H<sub>2</sub> due to the lower binding energies. Similar trend is also observed on all three surfaces for 1-propanol, suggesting that decomposition pathways are similar for both oxygenates. HREELS spectra confirmed the presence of

similar types of surface intermediates that contain the C–C–C–O skeletal structure on Mo(110) from the reaction of both molecules.

# 8.1.2 Catalytically Activating CO<sub>2</sub> using Ethane on Supported Bimetallic Catalysts

The second focus of this dissertation is mitigation of  $CO_2$  via catalytic  $CO_2$  reduction with widely available ethane, extracted from conventional natural gas and shale gas, to produce more useful feedstocks and value-added chemicals. Simultaneous transformation of  $CO_2$  and ethane offers advantages such as an increase in energy resources and a decrease in overall environmental footprints. However, for large-scale commercial processes for  $CO_2$  conversion, cost-effective and stable catalysts are necessary.

Catalytic performance of bimetallic catalysts, CoPt/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub>, NiMo/CeO<sub>2</sub> and FeNi/CeO<sub>2</sub>, is evaluated using a flow reactor at steady-states and GC was used to analyze gas products. It is observed that overall the catalytic stability is enhanced in all bimetallic catalysts, compared to the corresponding monometallic catalysts. TPR experiments show an increase in reducibility of active metals upon bimetallic formation. More importantly, this work has identified two types of supported bimetallic catalysts to promote the reactions of CO<sub>2</sub> and ethane. The first type consists of CoPt/CeO<sub>2</sub>, CoMo/CeO<sub>2</sub> and NiMo/CeO<sub>2</sub> for the dry reforming of ethane to produce synthesis gas through the C–C bond scission, while the second type includes FeNi/CeO<sub>2</sub> for the selective oxidative dehydrogenation to produce ethylene, CO and H<sub>2</sub>O through the C–H bond scission. Results from reactor studies agree with energy profiles on CoPt/CeO<sub>2</sub> and FeNi/CeO<sub>2</sub> predicted by DFT, which shows that on the CoPt(111) surface, the C–C bond cleavage of ethane to form CH<sub>3</sub>\*, CO\* and H<sub>2</sub>O(g) is

energetically more favorable compared to the selective C–H bond scission to form  $CH_2CH_2^*$ . On the other hand, DFT energy profile show that the FeNi(111) surface preferentially dehydrogenates ethane to form  $CH_2CH_2$ .

#### 8.1.3 Designing Non-precious Metal Hydrogen Electrocatalysts

The final chapter was devoted to designing non-precious metal hydrogen electrocatalysts with high activity in alkaline electrolytes. CO<sub>2</sub>-free hydrogen, produced from hydrogen electrolysis, can be used to catalytically activate CO<sub>2</sub> instead of direct utilization of hydrocarbons. A combination of DFT calculations and experimental electrochemical characterization provides an effective route for developing highly efficient and durable electrocatalysts. A volcano relationship is established for the hydrogen evolution reaction (HER) in alkaline medium by plotting the HER exchange current densities from electrochemistry measurements *versus* the hydrogen binding energy (HBE) from DFT predictions on monometallic surfaces. This volcano correlation suggests that the HBE can be used as a descriptor for the HER activity in alkaline medium, similar to the previously established correlation in acid medium.<sup>3</sup> It also suggests that HBE can be tuned by designing precious-metal-free bimetallic and multimetallic electrocatalysts. Based on this design principle, CoNiMo catalyst is found to have a remarkably enhanced activity compared to Ni.
#### 8.2 Future Work

### 8.2.1 Controlling Reaction Pathways of Multifunctional Unsaturated Oxygenates

This dissertation has studied the reaction pathways of C3 oxygenates such as propanal and 1-propanol as probe molecules on Ni- and Mo-based bimetallic surfaces. While results from Chapter 4 and 5 have provided valuable information regarding the C–O/C=O and the C–C bond scission, it is important to ensure that insights based on simple mononfunctional molecular surrogates on non-precious metal surfaces are transferable to the surface chemistry of more complex oxygenates. Hence, the next logical step for this part of thesis is to expand the study of the non-precious bimetallic surfaces to include multifunctional unsaturated oxygenates such as glyceraldehyde. Glyceraldehyde, with chemical formula  $C_3H_6O_3$ , is the simplest of all common aldoses – oxygenates which contain one or more OH groups and a single aldehyde group – and the molecular structure of glyceraldehyde is shown in Figure 8.1.



Figure 8.1 Molecular structure of glyceraldehyde

Glyceraldehyde has been used as a surrogate for glucose, building blocks of biomass, in fundamental studies on precious metal surfaces such as Pd(111) and Zn/Pt(111).<sup>79,161,162,163</sup> However, UHV studies are extremely limited due to the low vapor pressure of solid glyceraldehyde which requires the molecular beam dosing system to introduce the sample into the UHV chamber. McManus *et al.*<sup>161</sup> has shown

from DFT, TPD and HREELS that on Pd(111), glyceraldehyde adsorbs with an  $\eta^2$  configuration which forms  $\alpha$ -oxo- $\eta^2$  surface intermediates through an O–H bond scission. It is particularly interesting how admetal modification of non-precious metal surfaces such as Ni(111) and Mo(110) affects the C=O and the C–C bond scission of glyceraldehyde. Additionally, the results from the glyceraldehyde study are necessary to confirm the feasibility of controlling reaction pathways of more complex oxygenates on bimetallic surfaces.

### 8.2.2 Extending the Study of CO<sub>2</sub> Activation with Ethane

#### 8.2.2.1 Effect of Synthesis Methods

All supported bimetallic catalysts investigated in this thesis were synthesized using the co-impregnation synthesis method as mentioned in Chapter 2. In general co-impregnation synthesis is known to maximize the extent of bimetallic bond formation, compared to sequential synthesis.<sup>138</sup> It has been shown that for DRM on Ce-Pt/ZrO<sub>2</sub>, the co-impregnated catalysts have higher activity and resistance against carbon formation than the sequentially-impregnated catalyst due to stronger interaction between Ce and Pt which leads to an enhanced oxygen storing property of the catalyst.<sup>164</sup> However, in the case of partial oxidation of methane, introduction of Pt to Ni catalysts sequentially enhances the catalytic performance by forming mostly Pt-terminated sites, thereby reducing the extent of Ni oxidation in the presence of oxygen.<sup>165</sup> Hence it is important to investigate the effect of sequential *versus* co-impregnation synthesis on the catalytic activity.

Furthermore, the calcination temperature during synthesis is also important in determining the catalytic performance. Lower calcination temperature results in

insufficient interaction between the metals, while calcination at high temperature leads to sintering of metal particles.<sup>121</sup> For example, supported NiPd catalysts for DRM showed the highest activity at a calcination temperature of 600 °C, compared to other temperatures such as 200, 400, and 800 °C.<sup>166</sup> In this dissertation, calcination temperature of 290 °C is used to be consistent with previous studies.<sup>15</sup> Further studies on the effect of variations in calcination temperature are necessary to optimize the catalytic performance.

## 8.2.2.2 In-situ Characterization of Supported Bimetallic Catalysts

The main characterization techniques for supported catalysts used in this work are CO chemisorption and TPR to compare the number of active sites and the reducibility of active metals in supported catalysts, respectively. Although these techniques help to quantitatively compare the activity and the alloy formation of the bimetallic catalysts, more powerful characterization techniques are required to characterize the atomic arrangement of the catalysts under *in-situ* conditions. One powerful technique to characterize the local atomic and electronic structures of catalysts under *in-situ* conditions is X-ray absorption spectroscopy (XAS). Measurements of both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions of catalysts provides important information such as oxidation states, coordination numbers and bond distances.<sup>6</sup> For instance, XANES experiments show that Mo<sub>2</sub>C is oxidized to form MoO<sub>2</sub> when exposed to CO<sub>2</sub> and ethane, leading to deactivation since the active carbidic phase is necessary for higher activity. *In-situ* EXAFS studies have shown that under aqueous phase reforming (APR) conditions, supported NiPt bimetallic catalysts are Ni-terminated which leads to higher reforming activity.<sup>167</sup> In addition to XAS, diffuse reflectance infrared Fourier transform

spectroscopy (DRIFTS) can also be used for characterization of catalysts and/or adsorbed species under reaction conditions. DRIFTS measures the reflection of the IR light from the catalyst and is more surface-sensitive than transmission FTIR. Detailed description of DRIFTS can be found in this review.<sup>168</sup> A combined use of *in-situ* XAS, DRIFTS and time-resolved X-ray diffraction (XRD) can provide more complete structural and electronic information, critical for mechanistic studies, and for constructing relevant model surfaces in DFT calculations and UHV studies.

## 8.2.2.3 Effect of CO<sub>2</sub> Addition on Catalytic Activity

The partial pressure of CO<sub>2</sub> can significantly affect the catalytic activity and stability. Shen *et al.* observed that on Ga<sub>2</sub>O<sub>3</sub>/HZSM-5, increasing amount of CO<sub>2</sub> can positively affect the CO<sub>2</sub> conversion via RWGS on catalyst surface and negatively affects the conversion of ethane by replacing adsorbed ethane on the catalyst.<sup>127</sup> The same study also showed that the addition of CO<sub>2</sub> increases the stability via the reverse Boudouard reaction.<sup>127</sup> This phenomenon has also been seen in previous work for DRM.<sup>119</sup> In this work, CO<sub>2</sub> and ethane at an equimolar ratio is consistently used. Further studies should be performed to determine the effect of CO<sub>2</sub> addition on the catalytic activity of bimetallic catalysts supported on CeO<sub>2</sub> by varying the CO<sub>2</sub>/ethane ratio.

## 8.2.2.4 Reaction Mechanisms and Kinetic Studies

The focus of this work on supported catalysts in Chapter 6 has been mainly to identify low-cost and stable catalysts for both DRE and ODEC pathways. Reaction mechanisms and kinetic studies have yet to be fully determined to provide more information on the catalyst design and also to minimize deactivation. Currently, detailed and conclusive kinetic studies are limited for the reactions of  $CO_2$  and Ethane. Even for

the most widely studied DRM over precious metal catalysts, varying conclusions regarding the kinetics have been reported based on different ranges of reaction conditions such as temperature and pressure.<sup>121</sup> All factors such as the type of catalysts, the nature of supports, the interaction between the active metal and support have been shown to play an important role in determining the reaction and deactivation mechanism.<sup>121</sup> The interested reader is invited to read an excellent recent review on deactivation and regeneration.<sup>169</sup>

## 8.2.3 CO<sub>2</sub> Reduction with Higher Hydrocarbons

As previously discussed in Chapter 6, catalytic oxidative dehydrogenation of hydrocarbons with  $CO_2$  has major advantages such as lower energy requirements, and reduced greenhouse gas emission.<sup>18,132</sup> The results from Chapter 6 can be further applied to converting butane ( $C_4H_{10}$ ) and isobutane ( $i-C_4H_{10}$ ) into C4 olefins such as butenes ( $C_4H_8$ ), isobutene ( $i-C_4H_8$ ) and 1,3-butadiene (BD), all of which are industrially important chemicals, using  $CO_2$  as a soft oxidant. Thermodynamically, reactions of  $CO_2$  and C4 alkane are more favorable, compared to ethane. However, very limited studies have been performed for  $CO_2$ -ODH processes for C4 olefins synthesis due to challenges associated with rapid deactivation and lower selectivity.<sup>170</sup> Although challenging, this area of research opens up ample research opportunity to explore.

# 8.2.4 Theoretical Investigation of Electrolyte Effects

The correlation between reaction kinetics and metal surface properties has been crucial in identifying efficient and stable bimetallic hydrogen electorcatalysts in acid and alkaline media as discussed in Chapter 7.<sup>4, 160</sup> While powerful, the use of DFT to predict hydrogen binding energy on model surfaces is inadequate to model complex

electrochemical systems such as the structure of the electrochemical solid-liquid interface, the influence from water or  $H^+/OH^-$  in the electrolyte and the electric potential.<sup>171, 172</sup>

For instance, Durst *et al.*<sup>173</sup> studied the effect of pH on HOR/HER rates on Pt, Ir, and Pd carbon-supported catalysts and showed that the HBE is the unique and sole descriptor for the HOR/HER in alkaline electrolytes, confirming the main conclusion from Chapter 7. This result is also supported by the recent study which investigated experimentally measured HBE for polycrystalline platinum in a wide range of electrolyte pH from 1 to 13.<sup>174</sup> This study showed that the hydrogen binding energy, obtained from cyclic voltammograms, linearly increases with the pH. However, atomic scale simulation of the pH dependence of the HBE have yet to be explored. Extensive theoretical analysis is necessary for detailed mechanistic investigation regarding the HOR/HER mechanism to bridge the gap between the model systems and electrocatalysts under realistic operating conditions. The state-of-the-art modeling approaches can be found in the literature.<sup>171, 175, 176</sup>

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