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Reaction Pathways of Biomass-Derived Oxygenates on Noble Metal Surfaces

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Reaction Pathways of Biomass-Derived Oxygenates on Noble Metal Surfaces

Abstract
As the global demand for energy continues to rise, the environmental concerns associated with increased fossil fuel consumption have motivated the use of biomass as an alternative, carbon-renewable energy feedstock. Controlling reactive chemistry of the sugars that comprise biomass through the use of catalysis becomes essential in effectively producing green fuels and value-added chemicals. Recent work on biomass conversion catalysts have demonstrated the efficacy of noble metal catalyst systems for the reforming of biomass to hydrogen fuel, and the hydrodeoxygenation of biomass-derived compounds to value-added chemicals. In particular, Pt and Pd surfaces have shown considerable promise as reforming catalysts in preliminary aqueous phase reforming studies. It becomes important to understand the mechanisms by which these molecules react on the catalyst surfaces in order to determine structure-activity relationships and bond scission energetics as to provide a framework for engineering more active and selective catalysts. Fundamental surface science techniques provide the tools to do this; however, work in this field has been so far limited to simple model molecules like ethanol and ethylene glycol. Herein, temperature programmed desorption and high resolution electron energy loss spectroscopy are utilized in an ultra-high vacuum surface science study of the biomass-derived sugar glucose on Pt and Pd single crystal catalysts. Overall, it was determined that the aldehyde function of a ring-open glucose molecule plays an integral part in the initial bonding and reforming reaction pathway, pointing to the use of aldoses glycolaldehyde and glyceraldehyde as the most appropriate model compounds for future studies. Furthermore, the addition of adatom Zn to a Pt(111) surface was found to significantly decrease the C-H and C-C bond scission activity in aldehyde containing compounds, resulting in a preferred deoxygenation pathway in opposition to the decarbonylation pathway common on clean Pt(111). This has implications in the hydrodeoxygenation of biomass-derived compounds for the production of value-added chemicals like 2-methylfuran from furfural, or the catalytic upgrading of sugars. Ultimately, identification of the reactive mechanisms of biomass-derived molecules on different unique surfaces has lead to a greater understanding for what makes a more selective catalyst for specific chemical pathways.

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As the global demand for energy continues to rise, the environmental concerns associated with increased fossil fuel consumption have motivated the use of biomass as an alternative, carbon-renewable energy feedstock. Controlling reactive chemistry of the sugars that comprise biomass through the use of catalysis becomes essential in effectively producing green fuels and value-added chemicals. Recent work on biomass conversion catalysts have demonstrated the efficacy of noble metal catalyst systems for the reforming of biomass to hydrogen fuel, and the hydrodeoxygenation of biomass-derived compounds to value-added chemicals. In particular, Pt and Pd surfaces have shown considerable promise as reforming catalysts in preliminary aqueous phase reforming studies. It becomes important to understand the mechanisms by which these molecules react on the catalyst surfaces in order to determine structure-activity relationships and bond scission energetics as to provide a framework for engineering more active and selective catalysts. Fundamental surface science techniques provide the tools to do this; however, work in this field has been so far limited to simple model molecules like ethanol and ethylene glycol. Herein, temperature programmed desorption and high resolution electron energy loss spectroscopy are utilized in an ultra-high vacuum surface
science study of the biomass-derived sugar glucose on Pt and Pd single crystal catalysts. Overall, it was determined that the aldehyde function of a ring-open glucose molecule plays an integral part in the initial bonding and reforming reaction pathway, pointing to the use of aldoses glycolaldehyde and glyceraldehyde as the most appropriate model compounds for future studies. Furthermore, the addition of adatom Zn to a Pt(111) surface was found to significantly decrease the C-H and C-C bond scission activity in aldehyde containing compounds, resulting in a preferred deoxygenation pathway in opposition to the decarbonylation pathway common on clean Pt(111). This has implications in the hydrodeoxygenation of biomass-derived compounds for the production of value-added chemicals like 2-methylfuran from furfural, or the catalytic upgrading of sugars. Ultimately, identification of the reactive mechanisms of biomass-derived molecules on different unique surfaces has lead to a greater understanding for what makes a more selective catalyst for specific chemical pathways.
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Chapter 1. Introduction

1.1 Energy Requirements for a Growing World

Vast technological development has facilitated the continued growth in world population, and with it comes a quickly growing demand for energy and energy resources. In a 2013 report by the U.S. Energy Information Administration, projections for world energy consumption in the next 30 years predict an increase of 56 percent, from 524 quadrillion BTU in 2010 to 820 quadrillion BTU in 2040.\(^1\) Interestingly, the current world energy consumption profile is dominated by fossil fuel consumption (at approximately 80 percent of all energy media consumed), though it is the slowest growing energy source. Petroleum and other liquid fuel consumption grow at an annual rate of 0.9 percent contrasting with the increase in total energy demand of 1.5 percent.\(^1\) This discrepancy, partly due to the depletion of easy-to-access oil reserves and the need to access the more expensive deep sea wells and oil-shale reserves, has prompted the necessity for developments in other energy feedstocks. Natural gas and coal are globally attractive as alternatives to petroleum feedstocks, however these fail to also address the growing concern of environmental effects resulting from fossil fuel consumption and CO\(_2\) emissions.\(^2\)

Unfortunately, no single panacea exists to appropriately address the world energy challenge, and as such, meeting future global energy demands requires a multifaceted approach with a diverse global energy profile. In addition to the supply of traditional energy feedstocks, awareness in smart energy usage needs to be spread, breakthroughs in
energy technology and efficiency need to be shared and implemented, and most importantly, implementation and advancement of renewable energy alternatives must be realized. Frontrunners of the renewable energy technologies include solar (whether it be photovoltaics or solar thermal), wind, and biomass. Biomass stands out as a particularly interesting renewable energy feedstock because it is the only renewable source of carbon. This offers a unique solution for shorter term energy needs in that normal liquid fuels common to the current energy infrastructure can be produced in an emissions-conscious way, while energy storage technology catches up to the advancements in solar and wind renewables. By developing and implementing these alternative energy feedstocks along with the current energy profile, it is possible to safely and economically meet our growing global energy needs.

1.2 Biomass as an Energy Feedstock

As stated above, biomass is a carbon renewable energy feedstock with burgeoning potential for integration with the current world energy infrastructure. By definition, biomass is any organic matter that has the capacity to be converted into fuel; though by common convention it is most often associated with plant matter. The use of nearly any plant matter fits within the regime of biomass processing for energy production; however, the most economic biomass candidate sources have been identified as corn stover, wheat straw, switchgrass and sugarcane. These biomass sources are able to provide renewable carbon due to the fact that photosynthesis generated all of their carbonaceous plant mass from atmospheric CO₂ during the life and growth of the respective plant. As such, any fuel produced from biomass that is combusted to yield CO₂ has no net carbon
release to the atmosphere from the biomass. Furthermore, the use of biomass as a fuel can even become carbon negative if the roots are processed into a charcoal that is buried underground. Environmentally, this makes biomass an extremely attractive candidate for a renewable energy feedstock, which has driven developments in the field of biomass processing for fuel production.

Before examining the methods by which energy can be extracted from these sources of biomass, it is useful to understand the biomass composition. Generally, biomass is comprised of three major fractions: cellulose, hemicellulose, and lignin. Cellulose, the largest of the three fractions, is a straight chain polymer of glucose monomer repeat units, or more specifically a repeating glucose dimer (cellobiose) bound through \( \beta-1,4 \) glycosidic linkages, as seen in Figure 1.1. This fraction, making up between 35-50% of the dry biomass, is the most ordered, structurally sound fraction, and valuably yields a uniform glucose product when hydrolyzed.\(^3\)

![Figure 1.1: Molecular schematic of cellulose given by cellobiose repeat unit (public domain image).](image)

The next largest biomass fraction, making up 20-40% of the dry biomass, is the hemicellulose fraction. Hemicellulose is comprised of a randomly oriented, branched chain polymer of xylose, glucose, galactose, arabinose, mannose and a few other C\(_5\) and
C₆ sugars. Typically, hemicellulose contains a majority of xylan chains originating from repeating xylose units, though its composition varies greatly between different types of plants.³ Due to its random structure and amorphous character, hemicellulose can be easily hydrolyzed to yield a mixture of its composing sugars. The third largest fraction of biomass, comprising 15-25% of the dry biomass, is lignin. Lignin, unlike the cellulose and hemicellulose fractions, is not comprised of a series of carbohydrates, but rather is a highly branched, heterogeneous polyphenolic complex.³,⁵ The high degree of aromaticity and crosslinking in lignin make it far more difficult to process into useful components compared to the cellulose and hemicellulose fractions. Other than these three main fractions (cellulose, hemicellulose and lignin), the balance of the dry biomass is composed of a small quantity of minerals, resins, salts, fats and fatty acids.

Figure 1.2: General biomass fuel processing cycle. Biomass composition reflects approximate percentages of dry biomass fraction available for conversion.
In order to process biomass into useful fuels and chemicals, first it must be separated into its main fractions and broken down into their respective constituent molecules. Two chemo-mechanical methods common for the fractionation of biomass include biomass pulping and steam explosion fractionation,\textsuperscript{6-9} which separate the biomass into its cellulose, hemicellulose and lignin fractions. The less valuable, more difficult to process lignin fraction can be pyrolyzed into acidic pyrolysis oils\textsuperscript{10} that can later be used to generate heat and steam for the cellulose reformers. The cellulose and hemicellulose fractions of biomass can be hydrolytically broken down into their respective monomeric sugars by several techniques, the two most popular being enzymatic hydrolysis and acid hydrolysis. Enzymatic hydrolysis uses bacterial enzymes to digest the cellulose and hemicellulose.\textsuperscript{11} This process, however, is a time and space intensive operation, and often results in an industrial preference for alternative hydrolytic techniques. Acid hydrolysis uses strong (often sulfuric) acids to break the glycosidic $\beta$-linkages of the cellulose and hemicellulose compounds into their respective sugars,\textsuperscript{12} and is the preferred industrial method for cellulose processing.

Once isolated, the cellulosic sugars can be converted into various fuels using a number of different methods. One of the more popular processes for converting cellulosic sugars into fuel is through the fermentation process. In fermentation, yeast cells metabolize the isolated sugars, converting them into simple alcohols. The main alcohol that is produced is ethanol, which can later be distilled from the fermentation bath and used as a fuel or fuel additive. Currently, ethanol can be used directly as an internal combustion engine fuel additive or as the entire fuel itself in special ethanol ready
combustion engines. Unfortunately, ethanol does not have a high energy density so it cannot be used in jet fuel, nor is it particularly efficient in pure ethanol vehicles. Two of the major pitfalls of the fermentation processing method are the energy intensive distillation process necessary to isolate the ethanol from the fermentation bath, making the final product more expensive, and also the fuel flexibility. Because fermentation only produces simple alcohols, it becomes prohibitive when the desired products are more energy-dense liquid fuels.

An alternative method for the processing of the cellulosic sugars is a direct catalytic conversion route known as biomass reforming. In biomass reforming, the cellulosic sugars are broken down into synthesis gas (or syngas for short), a unique combination of hydrogen and carbon monoxide.\textsuperscript{13} Syngas can be used for a variety of different chemical processes or separated for use directly as a fuel. One common use for syngas is to react it with water, producing additional hydrogen and CO\textsubscript{2}, which can then be separated and the hydrogen passed through a fuel cell to produce clean electricity. Alternatively, the syngas can be used in a Fischer Tropsch process to produce “green” liquid hydrocarbons for use in the same way as a petroleum liquid fuel. Furthermore, the syngas can be used in numerous chemical processes to aid in the production of value added chemicals in various niche markets. Ultimately, reforming of biomass sugars is an extremely versatile route for renewable fuel and chemical production, however, the process by which these sugars are converted require active and selective catalysts to facilitate the conversion chemistry, and it demands a considerable amount of research to make this renewable technology competitive with traditional petrochemical sources.
1.3 Biomass Catalysis for Renewable Hydrogen

1.3.1 Motivation
Hydrogen is a clean and energy rich fuel that can be utilized with extremely high efficiencies in current fuel cell technology or with great versatility in Fischer Tropsch processes. Hydrogen fuel modalities are recognized as a tract for positive energy reform for a clean energy future; however, over 90% of industrial hydrogen is currently produced by reforming natural gas, resulting in a net contribution to atmospheric CO$_2$ and perpetuation of the detrimental greenhouse effect. Since there are no natural reserves of hydrogen on earth, new methodologies for hydrogen production must be explored to circumvent the use of natural gas. As noted above, biomass reforming is one possible route to the production of environmentally friendly, carbon-neutral hydrogen. This catalytic method can be approached in a number of different reaction paradigms, all of which require a fundamental understanding of the catalytic chemistry of cellulosic oxygenates. In the following sections, the different approaches for catalytic hydrogen production from biomass will be explored.

1.3.2 Methods for Biomass Reforming: Bio-Alcohol Steam Reforming
One route for the production of hydrogen from biomass is to use alcohols produced from biomass fermentation (methanol and ethanol) in place of natural gas during the steam reforming process. In this way, the same technology implemented for steam reforming of methane, for example, can be applied instead to a volatile, renewable bio-alcohol. One of the ancillary benefits of this method is that, unlike natural gas, which can be expensive to store and ship, the bio-alcohols methanol and ethanol can be stored easily as liquids.
The current state of the steam reforming of methanol and ethanol science hinges upon active and selective catalyst development. Ideally, the best catalyst performance would have a high activity for hydrogen production and selectivity for CO₂ and CO over CH₄ or coke formation. For methanol steam reforming, one of the most popular catalysts utilized is a Cu metal supported on ZnO.¹⁶, ¹⁷ This very active and selective catalyst is unfortunately pyrophoric and prone to deactivation,¹⁸ prompting considerable research into catalyst alternatives. Some of the frontrunners for Cu/ZnO alternatives include Ni and Ni-Cu alloys¹⁹ on carbon supports, Pd and PdZn alloys on varied supports,²⁰ as well as Pt, Co and Ru based catalysts.²¹, ²² For ethanol steam reforming, similar catalysts are used, though the additional necessity for C-C scission favors the noble metal catalysts (Pd, Pt, Ru, and Rh).²³ Ultimately, the selection of the best alcohol steam reforming catalysts depends on a fundamental understanding of the catalyst active sites, reactive mechanisms and support effects, which arises from in depth surface science studies. Surface science studies that use model single crystal catalysts and surface spectroscopic techniques to probe reforming chemistry are one approach that has proven very useful in providing this mechanistic insight. As will be discussed in a later section, this approach will form the basis for the studies reported in this thesis.

Though steam reforming of bio-alcohols is well studied and shares considerable technological overlap with the industrially mature natural gas steam reforming process, one of the major pitfalls is the fact that ethanol can already be (and is) utilized as a fuel or fuel additive. Further processing of bio-ethanol into hydrogen imparts additional process efficiency losses, which ultimately make the final product more costly. It would be far
more beneficial to utilize a reforming process that is fed with the biomass-derived sugars rather than the alcohols created by the fermentation of those sugars. In this more direct catalytic reforming method, the time and energy intensive fermentation process can be circumvented.

1.3.3 Methods for Biomass Reforming: Cellulosic Sugar Reforming

Alternative to the reforming of natural gas or bio-alcohols, the catalytic conversion of biomass-derived sugars directly to syngas provides a considerable potential for lucrative, renewable hydrogen production. Active and selective reforming of cellulosic sugars like glucose and xylose could transform global hydrogen production into a low carbon-emissions technology, and as such, a bulk of this thesis is focused on understanding the catalysts and catalytic mechanisms to do so. Due to the fact that many of the cellulosic sugars are solids with low vapor pressures, one of the principal challenges is finding media with which to facilitate their catalytic reactions. Two approaches studied thoroughly are aqueous phase reforming (APR)\textsuperscript{24,25} and ionic liquid reforming,\textsuperscript{26,27} both working on the principle of solubilizing the sugars before passing them over catalytic surfaces.

Ionic liquids are an interesting prospect for biomass processing because of their ability to solubilize difficult molecules, their low volatility, and their corresponding ease of separating phases. One very intriguing advantage of ionic liquids is that they can be used to not only dissolve sugars like glucose, but can go back a step and dissolve whole cellulose.\textsuperscript{27} By using hydrophilic ionic liquids like 1-butyl-3-methylimidazolium chloride, cellulose can be dissolved and passed over catalysts for reforming chemistry.
Though the prospect of dissolving whole cellulose is attractive, better results in reactive chemistry are achieved when using the cellulosic monomers like glucose. In a study on the reforming of glucose on a Ru-based homogeneous catalyst, glucose was dissolved in 1-ethyl-3-methylimidazolium acetate and a few other ionic liquids and reacted with a \([(p\text{-cymene})\text{RuCl}_2\)]_2 catalyst complex, producing modest hydrogen yields from sequential dehydrogenation reactions.\(^{28}\) Unfortunately, the current state of biomass reforming in ionic liquids is not yet economical, and has several major problems to address. Though recycling of ionic liquids is very plausible, initial production of these solvents is expensive and environmentally detrimental. Additionally, long term toxicology of ionic liquid use needs to be further investigated. These factors together generally favor the alternative method for cellulosic sugar reforming, APR.

Aqueous phase reforming utilizes the mild solubility of sugars like glucose in water to create an aqueous sugar stream that can be flowed through a catalyst filled reforming reactor, producing hydrogen given by the general reaction shown in equation 1.1.

\[
\text{C}_6\text{H}_{12}\text{O}_6(aq) \xrightarrow{\text{catalyst}} \alpha\text{H}_2 + \beta\text{CO} + \gamma\text{CO}_2 + \delta\text{H}_2\text{O} + \varepsilon\text{CH}_4
\]  

Furthermore, any CO that is formed can undergo a water-gas shift reaction to produce additional hydrogen and CO₂, given by equation 1.2.

\[
\text{CO} + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{H}_2 + \text{CO}_2
\]  

The product stream can then be passed through a liquid-gas separator, the gas effluent going on to a H₂ – CO₂ separator and all reusable streams going into their respective recycle loops.\(^{24}\) Some of the major advantages associated with APR as a hydrogen
production method include that high purity H₂ can be formed at high pressures (15 – 20 bar) without the energy intensive vaporization of water, and that any alkane byproducts formed can be separated and combusted for recycled heat generation.²⁵, ²⁹

With a general method in place, maturation of the APR process to economic feasibility is dependent on process yield and efficiency, factors largely motivated by appropriate catalyst selection and optimization. In an effort to elucidate the most effective APR catalysts, Dumesic et al.³⁰⁻³⁶ have contributed thorough catalyst screenings using model APR systems. In particular, using the polyol ethylene glycol as a model molecule to emulate cellulosic oxygenates, they were able to show that of several common group 8 – 10 metal catalysts supported on silica, reforming activity followed the trend of Pt ~ Ni > Ru > Pd ~ Rh > Ir with Pd and Pt metals showing the highest hydrogen selectivity and Ni, Rh and Ru showing low hydrogen selectivity.³⁰ Together, these results suggested that both Pt and Pd were very promising monometallic catalysts for biomass reforming via APR. Furthermore, in a follow-up study using Pt as the metal catalyst, comparisons were drawn between different support materials with regard to reforming activity and selectivity. Using TiO₂, Al₂O₃, SiO₂, SiO₂-Al₂O₃, ZrO₃, CeO₂, ZnO and carbon supports, the most active and selective catalysts were found to be Pt/Al₂O₃ and to a lesser extent, Pt/ZrO₃ and Pt/TiO₂.³⁴ Ultimately, they concluded that determining the best catalysts came down to identifying the catalytic factors necessary to control C-C scission with respect to C-O scission and hydrogenation reactions.

In an effort to extend the APR work on the model ethylene glycol system to a more appropriate biomass-derived sugar, Davda and Dumesic²⁴ solubilized glucose and
sorbitol (colloquially known as “reduced glucose”, seen in Figure 1.3) in an aqueous stream and passed it over a Pt/Al₂O₃ catalyst. Their findings indicated that hydrogen selectivity would be favorably improved if the glucose molecule was first hydrogenated to sorbitol at low temperatures before being passed into the higher temperature reforming reactor, though proof of concept was demonstrated for the use of glucose in APR. Again, using catalysis as a means to control relative bond breaking chemistry becomes crucial in achieving optimal activities and selectivities, in this case initially favoring hydrogenation over C-C and C-O bond scission in order to produce sorbitol for higher reforming yields.

![Molecular structure of (left) D-glucose and (right) sorbitol (reduced glucose)](image)

**Figure 1.3: Molecular structure of (left) D-glucose and (right) sorbitol (reduced glucose)**

Though the results presented above are promising for the production of hydrogen from cellulosic oxygenates via APR using monometallic catalysts, the use of expensive noble metal catalysts like Pt and Pd are not economically ideal. Motivated by this, Huber et al. have shown that by implementing less-costly bimetallic catalysts, favorable activities and selectivities can be achieved. Through the modification of Ni catalysts with Sn, activities and selectivities for hydrogen production in the APR of ethylene glycol, glycerol and sorbitol were found to approach those of the Pt/Al₂O₃ with considerably decreased deactivation compared to plain Ni catalysts. Implementation of bimetallic catalysts can have many beneficial emergent-effects (effects beyond a linear combination
of the two individual metals), though understanding their role in modifying the catalyst active site and reactive mechanisms becomes difficult in simple reactor studies and calls for more in-depth analysis using fundamental surface science techniques. By studying catalytic systems using fundamental surface science methods and model systems, insight can be gained of how the cellulosic sugar adsorbs to well defined catalyst surfaces, what catalyst properties control bond scission, what role secondary metals play in the reactive chemistry for bimetallic catalysts, how molecular functionality influences reaction pathways and what kinetic requirements will maximize activity and selectivity.

1.3.4 Surface Science for Biomass Catalysis

In an effort to provide a greater depth and breadth to the knowledge base of the catalytic conversion of biomass for hydrogen production, several research groups have implemented fundamental surface science techniques using model systems to study reaction mechanisms and structure-activity relationships. By utilizing model systems including idealized single crystal surfaces, ultra high vacuum (UHV) environments, and simplified reagent molecules, surface science techniques like high resolution electron energy loss spectroscopy (HREELS) or x-ray photoelectron spectroscopy (XPS) can be used to gain reaction details inaccessible to normal reactor studies. By understanding reaction mechanisms, bond breaking sequences and adsorption phenomena, the governing properties that guide industrial catalyst design can be elucidated. Furthermore, model catalysts can be chosen to have well defined surface structures so that specific active sites can be identified.
In a parallel to the APR work on monometallic catalysts discussed above, Griffin et al.\textsuperscript{37} studied the adsorption and reaction of model compounds ethylene glycol and 1,2-propanediol on the hydrogen-selective Pd(111) reforming catalyst. These two diol compounds act as molecular probes to investigate the role of multiple alcohol functionalities during the adsorption and reaction of biomass-derived oxygenates (which are often polyols) on relevant reforming catalysts. Using temperature programmed desorption and high resolution electron energy loss spectroscopy, it was determined that adsorption was dominated by low-temperature, simultaneous hydroxyl hydrogen activation, resulting in the formation of dioxy intermediates for both ethylene glycol and 1,2-propanediol (displayed in Figure 1.4). For both intermediates, C-H scission was favored on the alkoxy bound carbons over C-O and C-C scission, resulting in a dehydrogenation pathway to glyoxal surface species upon an increase in thermal energy. Further temperature increase to 250 – 350 K resulted in C-C scission and additional dehydrogenation to form adsorbed CO and H\textsubscript{2}. The maintained barrier against C-O scission on the Pd(111) surface with respect to C-H and C-C scission explains the high selectivity for hydrogen seen in APR experiments on Pd catalysts,\textsuperscript{30} though the affinity for Pd to keep CO surface bound (and occupying active sites) can explain why Pd reforming activity in APR is low compared to Pt. Ultimately, this study indicates that in order to achieve good reforming selectivity, having adjacent catalyst sites capable of dehydrogenating and bonding hydroxyls while maintaining selectivity for C-C bond scission over C-O scission is crucial.
Working from the promising Pt catalyst, Skoplyak et al. investigated the effects of introducing a second metal to modify catalyst activity and selectivity for biomass-derived oxygenate reforming. Using ethanol and ethylene glycol as molecular probes for biomass-derived sugars, they characterized the reaction of alcohols on a Pt(111) catalyst surface modified by creating surface alloys with Ni, Co, Fe, and Ti. In particular, two types of near-surface alloys were created and are displayed in Figure 1.5, the first being a simple overlayer on the Pt(111) surface, denoted as M-Pt-Pt, and the second being a sandwich-like structure with a subsurface metal monolayer, denoted as Pt-M-Pt, where M can be Ni, Co, Fe or Ti. These structures (particularly for the Ni/Pt(111) systems) were identified using low energy ion scattering (LEIS), scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES), and were found to be attainable by changing the Pt surface temperature during physical vapor deposition of the second metal.
Using these surfaces and a battery of surface science techniques, including TPD, HREELS, and density functional theory (DFT) modeling, Skoplyak was not only able to determine a reaction pathway for the model oxygenates, but was able to work out a relationship between the electronic properties of the surfaces and their reforming activity. For all four bimetallic pairs studied, it was found that the surface monolayer (M-Pt-Pt) structure was more active for reforming chemistry of both ethylene glycol and ethanol than the subsurface monolayer (Pt-M-Pt) structure. Furthermore, a general trend was found in which there was an increase in reforming yield as the d-band center of the surface approached the Fermi level.\textsuperscript{42} Though the Ti-Pt-Pt and Fe-Pt-Pt surfaces had d-band centers closer to the Fermi level than the Ni-Pt-Pt surface (and consequently higher reforming yields), the Ni-Pt-Pt surface showed the best reforming selectivity while maintaining very high reforming activity, making it the best catalyst candidate. When dosing ethylene glycol and ethanol on the Ni-Pt-Pt surface, both molecules initially dehydrogenated at the available hydroxyls forming ethylenedioxy and ethoxide species, respectively. This shows a parallel to the mechanism reported by Griffin et al. on Pd(111)
described above, and further suggests that low temperature alcohol dehydrogenation is important in the catalytic reforming pathway of oxygenates.

In an effort to address the high costs of the noble metal Pt and Pd catalysts that have been shown to be so effective in biomass reforming chemistry, Weiting Yu et al. demonstrated the plausibility of instead using a tungsten carbide catalyst.\textsuperscript{46, 47} Tungsten carbide (WC) is a thermally resilient catalyst material that is two orders of magnitude less expensive than Pd and three orders of magnitude less expensive than Pt. In a series of TPD and HREELS experiments, Yu probed the chemistry of several C\textsubscript{2} oxygenates, including ethylene glycol, acetaldehyde, acetic acid and glycolaldehyde, on WC catalysts. Unfortunately, the WC surface was not active for reforming chemistry and instead preferentially C-O cleaved to form surface bound ethylene; however, modifying the WC surface with Ni atoms in a manner similar to the studies by Skoplyak et al. highlighted above dramatically altered the chemical pathway. By vapor depositing a Ni monolayer on the WC surface, the d-band center of the catalyst and subsequent binding energies of the reactants (both quantities being reported descriptors for reforming activity in simple oxygenates\textsuperscript{39-43}) approached that seen for the Ni-Pt-Pt catalyst,\textsuperscript{46} a surface shown to be extremely active and selective for the reforming of ethylene glycol and ethanol.\textsuperscript{42} Consequently, this Ni/WC catalyst behaved very much like the Ni-Pt-Pt surface, showing a high reforming activity, selectivity for O-H and C-C bond cleavage over C-O activation, and a reactive mechanism that formed alkoxide and dioxy intermediates similar to those seen on Ni-Pt-Pt and Pd(111) surfaces. Ultimately, the Ni/WC catalyst shows considerable promise for a possible oxygenate reforming catalyst, exhibiting
favorable reforming activities, low cost, and much better thermal stability compared to the metastable Ni-Pt-Pt surface.

The body of work on biomass reforming catalysis, though somewhat nascent, is rich with promise for the future. The foundations for a fundamental approach to biomass reforming catalyst design have been laid, and a number of key elements to the necessary bond scission pathways have been outlined. A focus on catalyst design for selective H₂ and CO formation has lead to the determination that amenable catalysts will preferentially dehydrogenate alcohol functions and form alkoxide and dioxy surface intermediates at low temperatures, followed by controlled C-H and C-C cleavage, all the while maintaining C-O character. Unfortunately, the majority of these surface science studies have been limited to work on small (C₁ – C₃) alcohols and polyols, and no confirmation has been provided that these molecules are appropriate model compounds for the larger cellulosic sugars like glucose and xylose. Furthermore, since the current body of work has been limited to small linear molecules, no considerations have yet been made to accommodate the possible ring structures that cellulosic sugars often adopt. Maturation of this technology demands additional study into cellulosic oxygenate reaction pathways and catalyst structure-activity relationships, as well as further exploration of promising new bimetallic systems.

1.4  Biomass Catalysis for Value Added Chemicals

1.4.1  Motivation
Alternative to biomass reforming chemistry, where the focus is on C-C and C-H activation, catalysis for the production of liquid fuels and value added chemicals hinges
on the retention of those very bonds. Control of selective deoxygenation chemistry can ultimately produce compounds from cellulosic sugars with high chemical value. For example, dehydration of xylose and glucose can produce furfural and 5-hydroxymethylfurfural (5-HMF), respectively, two platform molecules that have been identified as having extremely high potential for conversion to a variety of value-added chemicals and fuel additives. These two compounds are chemically versatile, and can be catalytically coupled using aldol-base condensation reactions to produce higher chain diesel fuel compounds, dehydrated to produce solvents, surfactants and nylon intermediates, deoxygenated to produce higher octane number gasoline additives and even undergo etherification to produce functional polymers. All of these chemical transformations unfortunately are non-trivial, and require a high degree of functional selectivity when it comes to catalytic bond breaking. To accomplish this, advanced catalysts are needed that take advantage of structure-activity relationships and intermediate stabilization, characteristics that require an in-depth body of surface science research to identify and understand.

![Molecular schematics of value-added platform chemicals (left) furfural and (right) 5-hydroxymethylfurfural (5-HMF).](image)

Figure 1.6: Molecular schematics of value-added platform chemicals (left) furfural and (right) 5-hydroxymethylfurfural (5-HMF).
1.4.2 Catalytic Hydrodeoxygenation

As mentioned above, it is highly desired to gain a selective catalytic control over the transformation of biomass-derived compounds to useful fuels and chemicals. One of the major challenges is addressing the high oxygen content and over-functionalization of these platform molecules. If these molecules are to be used as chemicals, fuels and fuel additives, it becomes important to decrease the oxygen content, and one way to accomplish this is through selective hydrodeoxygenation or HDO. By leveraging the benefits of bimetallic catalysis, favorable chemistries can be achieved.

One such example of the use of bimetallic catalysts for a relevant HDO reaction is the use of a Ni-Cu bimetallic catalyst for the conversion of biomass-derived platform molecule furfural (described above and pictured in Figure 1.6) to cyclopentanone. Cyclopentanone is an important chemical building block used for the pharmaceutical industry, rubber production, and insecticide production. By reacting furfural over a Ni-Cu catalyst supported on SBA-15, HDO selectivity to cyclopentanone was dramatically increased to 62% at 98% conversion from 0% at 62% conversion on Cu/SBA-15 and 39% at 42% conversion on Ni/SBA-15 monometallic catalysts.

Another example of the use of bimetallics to promote HDO chemistry in biomass-relevant molecules is the HDO of the lignocellulosic compound \( m \)-cresol to toluene and methylcyclohexane. Do et al. has demonstrated that modification of an alumina supported Pt catalyst with Ni or Co metals can greatly increase HDO activity. In particular, conversion of \( m \)-cresol to HDO products toluene and methylcyclohexane increased from 38.3% on Pt/Al\(_2\)O\(_3\) to 56.7% on Pt-Co/Al\(_2\)O\(_3\) and to 62.7% on Pt-Ni/Al\(_2\)O\(_3\). From these
studies, it is clear that the emergent effects of bimetallic catalysts can greatly influence the desired HDO chemistry; however, the mechanisms by which these chemistries occur must be further understood if future advancements are to be made. To do so, as was the case with biomass reforming chemistry, fundamental surface science studies can be utilized to develop a deeper understanding of how catalyst modification alters the reactive mechanisms of relevant bio-molecule HDO.

In one study performed by Sitthisa et al., density functional theory was utilized to elucidate the governing mechanism for a catalytic phenomenon seen in the reaction of furfural on Ni catalysts. When reacting furfural on SiO$_2$-supported Ni, the product distribution was dominated by the decarbonylation product, furan. However, when Fe was introduced to the Ni/SiO$_2$ catalyst, the selectivity dramatically changed favoring the deoxygenation product (via hydrogenolysis, displayed in Figure 1.8) 2-methylfuran. In particular, the selectivity for 2-methylfuran was ~0% on a Fe/SiO$_2$ catalyst and ~5% on the Ni/SiO$_2$ catalyst, but increased to over ~65% on the Fe-Ni/SiO$_2$ catalyst. This is relevant because the hydrogenolysis pathway retains additional carbon content compared to decarbonylation, resulting in the higher octane number, greater-valued product, 2-methylfuran. To understand this difference in reactivity, DFT modeling of the bonding configurations and energetics of furfural on the different catalyst surfaces was implemented. The DFT results show that addition of the oxyphilic Fe atoms to the Ni surface permit an $\eta_2$(C,O) aldehyde bonding configuration where the oxygen is strongly bound to an Fe atom in such a way that it increases the C-O bond length (corresponding to a weakening of the bond strength) compared to that seen on a pure Ni surface. This
energetically favors the deoxygenation pathway via C-O scission to yield 2-methylfuran, whereas on the Ni surface, the aldehyde C-O bond stays intact and instead forms an acyl intermediate via competing C-H scission, subsequently decarbonylating and yielding the less valuable furan product.\textsuperscript{54} From this work, it becomes clear that addition of a second oxyphilic atom to a catalyst surface can provide an oxygen bonding site that alters bond-scission energetics and can influence product distribution.

![Figure 1.7: Schematic of various oxygenate adsorption configurations including (a) $\eta_1(O)$, (b) $\eta_2(C,O)$, (c) acyl and (d) alkoxide.](image)

![Figure 1.8: Reactive pathway for furfural on (a) Fe-Ni/SiO$_2$ that undergoes hydrogenolysis to deoxygenate and form 2-methylfuran, and (b) Ni/SiO$_2$ that undergoes decarbonylation to furan.](image)

This study by no means is the only relevant investigation that shows how addition of a second metal can modify bonding configurations or reaction energetics. Nishiyama et al.\textsuperscript{59} have done work on the selective hydrogenation of unsaturated aldehydes like
crotonaldehyde showing that addition of Sn to a Rh catalyst alters the aldehyde bonding configuration to favorably retain the molecule’s C=C character while hydrogenating the aldehyde oxygen. This occurs because the aldehyde oxygen lone pair electrons preferentially donate electronic character to the locally electron deficient Sn sites, resulting in an upright $\eta_1(O)$ bonding configuration (shown in Figure 1.7a) that limits the C=C bond proximity to the surface. By understanding these catalytic nuances that lead to selective hydrogenation, more selective hydrodeoxygenation pathways can be explored.

If selective hydrodeoxygenation of biomass-derived oxygenates is desired, retention of C-C and C-H character is important. Zn-modification of group 10 metals has been demonstrated as one method to control the barriers to C-C and C-H scission for oxygen containing compounds. By using small additions of Zn to a Pd(111) surface, Jeroro et al. have shown that long range electronic effects modify catalytic activity, resulting in increased barriers for C-C and C-H scission for small (< C$_3$) alcohols and aldehydes. Similar to the Sn-Rh system discussed above for selective hydrogenation of unsaturated aldehydes, a Pt-Zn bimetallic system was shown by Ammari et al. to be highly selective for hydrogenation of the carbonyl group in crotonaldehyde. Using the concepts from both these Zn-containing systems, Martono et al. characterized oxygenate reactions on two Zn-Pt catalyst constructs, one as a near-surface PtZn alloy, and the other as a Pt(111) surface decorated with Zn adatoms. They demonstrated that the oxygenate intermediates formed on the Zn-adatom surfaces were stable to comparably high temperatures, showing increased barriers for C-C and C-H scission. Furthermore, they were able to demonstrate
using XPS that the oxyphilic Zn atoms acted as the initial site by which reagent oxygen atoms interacted with the surface.

Though these systems show promise for implementation in the field of hydrodeoxygenation chemistry, a great deal of research must still be conducted. Extensions to larger biomass-derived oxygenates are needed to elucidate the role of multiple alcohol functionalities in their reaction on these candidate bimetallic systems. Additionally, experimental study of the reaction mechanisms and catalytic active sites are needed to verify mechanistic claims purported by DFT calculations for adsorption configurations and bond breaking sequences. Furthermore, connections must be made that shed light on the role of electronic and surface structure effects originating from the addition of a second metal to a catalyst surface, and how they can be used to control HDO chemistry.

1.5 Thesis Objectives
With the goal to advance the science necessary for implementing biomass into the world energy infrastructure in an economically and environmentally conscious way, considerable research has been performed on numerous chemical platforms. Advances in reforming and hydrodeoxygenation catalysis have highlighted the favorable activities and selectivities of noble metal mono- and bi-metallic catalysts. Unfortunately, many simplifications and generalizations had to be made, including the functional emulation of biomass molecules with simple compounds, in order to lay the groundwork for this research. Furthermore, a greater mechanistic understanding of these catalytic systems was shown to be needed in order to elucidate the properties that govern favorable catalytic
characteristics, such to guide future catalyst development. It was thus the objective of this thesis to address some of these problems by taking a three aim approach listed below, utilizing the tools of fundamental surface science as a means to illuminate the catalytic reaction pathways of biomass-derived oxygenates.

The first aim of this thesis was to identify the characteristics of an appropriate model compound in surface science studies of cellulosic sugars. Prior to the work presented herein, all UHV surface science studies on biomass reforming had utilized simple C$_1$-C$_3$ alcohols and polyols as molecular surrogates, citing the complexity of using actual biomass-derived sugars as a prohibitive factor. The initial goals of this thesis were to demonstrate that the cellulosic sugar glucose can, in fact, be utilized when appropriate apparatus configurations are implemented, and to identify what the major chemical functionalities are (and subsequently identify the best model compounds) in the adsorption and reaction of glucose on relevant noble metal catalysts Pt(111) and Pd(111).

The second aim of this thesis was to probe the pathway for catalytic reforming of glucose. APR data on Pt- and Pd-based catalysts have shown promising activities and selectivities for the reforming of glucose and related compounds; however, the mechanism by which the molecules react on the catalyst surfaces was not well understood. By using fundamental surface science methods, the reactive mechanisms were elucidated and the bond scission sequences determined, elements that are extremely useful in indentifying properties that make an effective catalyst. Furthermore, extension of the research on the favorable reforming chemistry seen with the Ni-Pt-Pt and Pt-Ni-Pt
bimetallic system\textsuperscript{39-43} to the Ni-Pd-Pd and Pd-Ni-Pd bimetallic system was investigated, as the Pd-based catalyst is less expensive and touts higher hydrogen selectivities.

The third aim of this thesis was to investigate the mechanisms that mediate HDO selectivity in bimetallic catalysts. In particular, it was of interest to determine the validity of the DFT predicted mechanism for the deoxygenation of aldehyde functionalities on group 10 metals modified with a second oxyphilic metal.\textsuperscript{54} This was done using the promising Zn/Pt bimetallic catalyst and aldehyde containing model compounds acetaldehyde and glycolaldehyde. Furthermore, this aim set out to identify the possibility of HDO of biomass-derived sugars on the Zn/Pt system for the purpose of catalytic upgrading. Ultimately, the overarching objective of this thesis was to use fundamental surface science techniques to identify how biomass-derived sugars mechanistically behave on different relevant noble metal catalysts for the purpose of fuel and chemical production.

1.6 Thesis Outline

The thesis presented herein is broken into eight separate chapters. Chapter 2 provides an explanation of the apparatuses used throughout the studies described in this thesis and the principles behind their operation, as well as descriptions of sample preparations. Chapter 3 demonstrates the first implementation of glucose in a surface science study and, along with parts of Chapter 4, outlines the most appropriate compounds for use as biomass sugar model surrogates. Chapters 4 and 5 identify the reaction pathways and general reactivity of glucose, glyceraldehyde and glycolaldehyde on Pd and Ni/Pd bimetallic catalysts. Chapters 6 and 7 identify the mechanism for HDO of aldehyde containing
compounds and biomass-relevant molecules on the Zn/Pt bimetallic system for the purpose of value added chemical production. Finally, Chapter 8 will summarize the major conclusions drawn within each of the major sections of this thesis.
Chapter 2. Experimental Methods

2.1 Introduction

As described above, experimentation under the controlled, ultra-high vacuum environment affords a myriad of spectroscopic techniques for the characterization of catalytic surfaces and reaction mechanisms. The vacuum environment also allows surfaces to remain clean for extended periods of time while spectroscopic techniques are being performed. To further illustrate this, it is instructive to do a brief calculation of the time it would take for every atom of a catalyst surface to participate in a collision with a gaseous N\textsubscript{2} molecule at ultra-high vacuum (UHV) pressure and at atmospheric pressure.

Drawing from the kinetic theory of gases, we can start with the equation for collision frequency of gas molecules with a surface,

\[ \Phi = \frac{1}{4} n v_{rms} \]  \hspace{1cm} (2.1)

where \( \Phi \) is the collision rate in molecules per cm\textsuperscript{2} per second, \( n \) is the number of molecules per unit volume, and \( v_{rms} \) is the average speed of the gas molecules given by

\[ v_{rms} = \sqrt{\frac{3k_bT}{m}} \]  \hspace{1cm} (2.2)

where \( k_b \) is the Boltzmann constant, \( T \) is temperature and \( m \) is the mass of the molecule. Combining equations 2.1 and 2.2, and applying the ideal gas law to represent the number of molecules per unit volume in terms of pressure and temperature, we arrive at

\[ \Phi = \frac{\sqrt{3} N_A}{4} \frac{P}{\sqrt{R} \sqrt{MW} T} \]  \hspace{1cm} (2.3)
where \( N_A \) is Avogadro’s number, \( R \) is the ideal gas constant, \( P \) is pressure, and \( MW \) is the molecular weight of the gas in question (28 g mol\(^{-1}\) for \( \text{N}_2 \)). The normal operating pressure for our ultra-high vacuum chamber is approximately 2 \( \times \) 10\(^{-10} \) Torr; plugging that value into equation 2.3 at room temperature (298 K) for \( \text{N}_2 \) gives a collision rate of

\[
\Phi(298 \text{ K}, 2 \times 10^{-10} \text{ Torr}) = 8.35 \times 10^{10} \frac{\text{molecules}}{\text{cm}^2 \cdot \text{s}}.
\]

Now that may seem like a lot of collisions with the catalyst surface, but if you consider a Pd(111) single crystal, the surface contains approximately 1.5 \( \times \) 10\(^{15} \) Pd atoms per cm\(^2\). Dividing that by our result for the ultra-high vacuum conditions collision rate calculated above, you find that it takes about 5 hours for all the atoms of the Pd surface to participate in a gas collision. That affords plenty of time for performing spectroscopic analyses of the catalyst surface. In comparison, doing the same calculation but instead of at ultra-high vacuum pressures, you use atmospheric pressure of 760 Torr, you find that it takes approximately 5 nanoseconds for all of Pd surface atoms to participate in a gas collision.

Having a clean, unperturbed catalyst surface allows for the characterization of reaction and adsorption mechanisms using techniques like temperature programmed desorption (TPD), high resolution electron energy loss (HREEL) spectroscopy, Auger electron spectroscopy (AES) and other methods that will be discussed in greater detail later in this chapter. Furthermore, this chapter will contain procedural descriptions for the preparation of unique catalyst surfaces utilized throughout this thesis.
2.2 Ultra-high Vacuum Apparatus

2.2.1 General Vacuum Chamber Configuration

The surface science studies described within this thesis were carried out in a UHV chamber represented below in Figure 2.1, maintained at a normal operating pressure of approximately $2 \times 10^{-10}$ Torr. The chamber vacuum was achieved by three stages of pumping whereby a mechanical rotary vane roughing pump (not shown in the figure) pumped the chamber down to $10^{-5}$ Torr from the outlet of a turbomolecular pump that was responsible for bringing the chamber down to $10^{-9}$ Torr, at which time the ion pump at the bottom of the chamber pumped the final stage, bringing the chamber to its operating pressure of $2 \times 10^{-10}$ Torr. To reach these pressures, the chamber had to be “baked out” or heated with electrical heating tapes at approximately $250^\circ$ C for a duration greater than 12 hours to desorb the rest gas that had adsorbed on the inside chamber walls while the chamber was open to the atmosphere. In situations where hard-to-pump molecules (like $\text{H}_2$) were introduced into the chamber during experiments, a quaternary pump, the titanium sublimation pump (not shown in the figure), was utilized for a short period of time to assist in lowering the chamber pressure.
Figure 2.1. Schematic of main ultra-high vacuum chamber used during the studies contained herein. The apparatus is shown from the front (a) and back (b).

Within the UHV chamber, catalyst sample preparation and analysis could be performed in one of two main sections, one above and coaxial to the other, as is visible in Figure 2.1. Within the top chamber section, a catalyst could be exposed to gaseous reagents through the variable leak valve (which is connected to a dosing line that will be described in greater detail in the next section), a second metal could be deposited onto the catalyst surface from the metal deposition feedthrough and monitored with an inline quartz crystal microbalance (QCM), the catalyst could be visibly monitored through a large quartz viewport, it could also be exposed to line-of-sight molecular beams produced in the high-vacuum effusion chamber (as will be discussed in a later section), the contents of the chamber atmosphere could be monitored for molecular cracks with an SRS
RGA200 quadrupole mass spectrometer, the catalyst surface could be cleaned with \( \text{Ar}^+ \) ion bombardment from a PHI electronics sputter gun, or the catalyst could be analyzed with the OCI Vacuum Engineering back display Low Energy Electron Diffraction (LEED) / Auger Electron Spectroscopy (AES) optics unit. Alternatively, the catalyst could be lowered in the Z-direction by the adjustable manipulator into the second, lower chamber section where it could be analyzed using the HREEL spectrometer from LK technologies.

![Catalyst crystal mounting schematic for a rectangular crystal geometry.](image)

**Figure 2.2: Catalyst crystal mounting schematic for a rectangular crystal geometry.**

Within the UHV chamber, the single crystal catalyst samples under study were configured as displayed in Figure 2.2. Extended inside the chamber from the top of the manipulator, an electrically insulated, UHV rated, stainless steel feedthrough with both copper power leads and chromel and alumel thermocouple leads supported the sample
mounting configuration. The ends of the copper power leads were tightly wrapped in a small amount of tantalum foil to allow spot-welding of thin tantalum mounting posts, as displayed in the figure. The back of the catalyst crystal was then spot-welded to the tantalum mounting posts for conductive cooling and resistive heating. To monitor the sample temperature during heating and cooling, chromel and alumel thermocouple wires were spot-welded to the top of the crystal and connected to their respective feedthrough leads. Heating the crystal to temperatures up to 1200 K could be achieved by passing 0-10 amps of current through the thin tantalum mounting posts from the copper power leads. Conductive cooling was achieved by filling the feedthrough cavity around the power leads with liquid nitrogen, effectively cooling the catalyst crystal to temperatures as low as 100 K.

2.2.2 Dosing Line Configuration

Controlled introduction of gaseous, liquid and some higher vapor pressure solid reagents into the UHV chamber was accomplished using the dosing line configuration displayed in Figure 2.3. Gaseous reagents like argon, for example, would be supplied from lecture bottles where mild pressures of the gas would fill the dosing line after the line was evacuated to approximately 20 mTorr by the piped in roughing pump. Pressures in the dosing line would be monitored by a thermocouple pressure gauge tube (Kurt J. Lesker), and the gases were leaked into the UHV chamber via the precision variable leak valve (MDC) capable of controlled leak rates of approximately $5 \times 10^{-10}$ Torr/s.
Figure 2.3: Dosing line configuration for the controlled introduction of reagents into the UHV apparatus. The interface with the UHV chamber is at the chamber mounted variable leak valve.

For the dosing of amenable liquids and solids, the glass bulb represented in Figure 2.3 would be used. Separated from the dosing line by a ball valve, high vapor pressure liquids contained in the glass bulb could be purified by repeated freeze-pump-thaw cycles whereby an external liquid N\(_2\) reservoir was used to freeze the contained liquid, followed by the opening of the ball valve, pumping on the frozen liquid with the roughing pump, closing of the ball valve and subsequent thawing of the frozen liquid. For most high vapor pressure liquids, by closing the needle valve to the roughing pump and lecture bottle section of the dosing line, the evacuated line above the glass bulb could be filled with sufficient reagent pressure simply by opening the ball valve while the liquid was at room temperature. If the reagent in the glass bulb was instead a low vapor pressure liquid or solid, both the bulb and above dosing line could be wrapped in electrical heating tape and heated in a controlled manner using a variable transformer and a type K
thermocouple for temperature monitoring. This would allow the dosing line to reach high enough temperatures to produce sufficient vapor pressure for dosing. If instead, the reagent was a solid that would decompose before reaching a temperature for sufficient vapor pressure (as is the case for glucose and glyceraldehyde) this dosing configuration could not be used, and instead the molecules were implemented in the high vacuum effusion chamber described in the following section. For reference, Table 2.1 lists how different compounds were introduced into the UHV environment during the course of the studies presented in this thesis.

Table 2.1: Dosing methods for compounds implemented throughout this thesis.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Dosing Method</th>
<th>(^a)Dosing Temp [(^{\circ})C]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gasses</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H(_2)</td>
<td>Lecture Bottle</td>
<td>n/a</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>Lecture Bottle</td>
<td>n/a</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O(_2)</td>
<td>Lecture Bottle</td>
<td>n/a</td>
</tr>
<tr>
<td>Argon</td>
<td>Ar</td>
<td>Lecture Bottle</td>
<td>n/a</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C(_2)H(_4)</td>
<td>Lecture Bottle</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Liquids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>CH(_3)OH</td>
<td>Glass Bulb</td>
<td>r.t.</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C(_2)H(_5)OH</td>
<td>Glass Bulb</td>
<td>r.t.</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>C(_2)H(_4)O</td>
<td>Glass Bulb</td>
<td>r.t.</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>CH(_3)CHOHCH(_3)</td>
<td>Glass Bulb</td>
<td>r.t.</td>
</tr>
<tr>
<td><strong>Solids</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetoin</td>
<td>C(_4)H(_8)O(_2)</td>
<td>Glass Bulb</td>
<td>150-155</td>
</tr>
<tr>
<td>Glycolaldehyde</td>
<td>C(_3)H(_6)O(_2)</td>
<td>Glass Bulb</td>
<td>50-65</td>
</tr>
<tr>
<td>Glyceraldehyde</td>
<td>C(_3)H(_6)O(_3)</td>
<td>HV Effusion Chamber</td>
<td>95-115</td>
</tr>
<tr>
<td>D-Glucose</td>
<td>C(_6)H(_12)O(_6)</td>
<td>HV Effusion Chamber</td>
<td>130-145</td>
</tr>
</tbody>
</table>

\(^a\)Temperatures ranged due to resting vacuum pressures. n/a not applicable. r.t. room temperature

2.2.3 **High Vacuum Dosing Chamber Configuration**

As described above, some compounds (namely glucose and glyceraldehyde) could not be suitably dosed using the traditional dosing line system via variable leak valve. The heating necessary to produce sufficient vapor pressure for the use of the dosing line (approximately 100 mTorr) for glucose and glyceraldehyde was in excess of their thermal...
degradation temperatures. For example, differential scanning calorimetry and thermal gravimetric analysis by Orsi\textsuperscript{67} show that glucose begins to thermally decompose at 165 °C; however, calculations for the enthalpy of vaporization of glucose by Suuberg et al.\textsuperscript{68, 69} require that glucose be heated to approximately 230 °C in order to produce a vapor pressure of 100 mTorr, well in excess of the temperature of thermal degradation. To address this problem, a special dosing apparatus was designed to accommodate the requirements for dosing low vapor pressure solids into a vacuum environment. To understand the parameters that the special dosing apparatus must operate within, it is instructive to map out the phase boundary for sublimation of glucose.

Drawing from chemical thermodynamics, the relationship between vapor pressure and temperature for a single component system (under the conditions where \( \Delta H^\circ_{\text{vap}} \) is constant) is given by the integrated Clausius-Clapeyron equation,

\[
\ln P = -\frac{\Delta H^\circ}{RT} + A
\]  

(2.4)

where \( P \) is the vapor pressure of the compound, \( \Delta H^\circ \) is the enthalpy of vaporization, \( R \) is the universal gas constant, \( T \) is the absolute temperature and \( A \) is a constant. Empirical data for the vaporization of several biomass-derived model compounds have been collected by Suuberg, Oja and Lilly\textsuperscript{69} using the Knudsen effusion technique, and can be applied with the Clausius-Clapeyron equation to produce the sublimation phase boundary curve for glucose seen in Figure 2.4. From this plot it is clear to see that at room temperature, glucose has sufficiently low vapor pressure (less than \( 1 \times 10^{-14} \) Torr) to remain in UHV conditions unperturbed, yet it can have sufficient vapor pressures for controlled dosing in UHV at temperatures below its thermal decomposition range.
(pressures on the order of $1 \times 10^{-7}$ Torr at 390-400 K, 38 K below the onset of thermal degradation). This indicates that a dosing apparatus maintained at pressures of $1 \times 10^{-8}$ Torr or below would be sufficient to maintain a supply of glucose for an extended period of time, while having the ability to heat the glucose to produce an appreciable vapor pressure for dosing without thermally degrading it. With these stipulations, an apparatus was created to facilitate controlled high-vacuum dosing, and is represented schematically in Figure 2.5.

![D-glucose Sublimation Phase Boundary](image)

**Figure 2.4:** Sublimation phase boundary for glucose as calculated from the Clausius-Clapeyron equation and empirical data from Suuberg et al. 

---

![Diagram of D-glucose Sublimation Phase Boundary](image)
Figure 2.5: Simplified schematic of the high-vacuum effusion chamber with an example Pd(111) crystal catalyst.

This high-vacuum effusion chamber consists of a UHV rated compartment isolated from the main UHV apparatus by a gate valve, which is pumped to high-vacuum pressures by a turbomolecular pump, and contains a resistively heated quartz effusion cell. The quartz effusion cell was comprised of a small, 5 mm diameter quartz glass tube, approximately 1 cm in length that was pinched off at one end. The pinched off end contained a small gap to allow for a thermocouple insert for temperature monitoring. The glass cell was suspended by a coil of tantalum wire that was spot-welded to two copper heating posts that supported the flow of current. Heating was done resistively by passing current through the copper posts and through the tantalum coil. The cell could be packed with the desired sugar powders, and was oriented in the direction of the gate valve.
Heating to the appropriate temperatures would create a molecular flux that could directionally impinge on the catalyst surface during the controlled periods when the gate valve was opened.

2.3 Sample Preparation

2.3.1 Cleaning Procedure

Within this thesis, two catalyst single crystals were utilized for study. The first was a Pt(111) single crystal (Goodfellow), 1 cm in diameter and 2 mm thick, the second was a Pd(111) single crystal (Princeton Scientific), 10 mm × 5 mm × 2 mm, both oriented within 0.5° of the crystal plane and of 5N purity. Each crystal was mechanically polished to a mirror finish on one side starting with a 15 μ diamond paste and successively proceeding to finer and finer pastes ending at a 0.5 μ paste. Polishing cloths included medium fine cotton for the larger size pastes, fine rayon for the medium size pastes and synthetic velvet for the smallest pastes.

Once polished, the crystals could be mounted and put in UHV conditions where they were cleaned by annealing and argon ion bombardment. A typical cleaning procedure included repeated cycles of 2 kV Ar⁺ ion bombardment (at an Ar pressure of 2 × 10⁻⁵ Torr) from the PHI sputter gun for 30 minutes, annealing in vacuum at 1100 K for 15 minutes, and annealing at 1100 K in 2 × 10⁻⁸ Torr O₂ for 20 minutes. In this way, sputtering was used to slough off the top most surface layers of the crystal that would be coated with impurities, annealing would be used to restructure the crystal surface and to draw carbon impurities to the surface, and annealing in O₂ would be used to burn off said carbon.
2.3.2  **Metal Depositions**

In addition to the Pt(111) and Pd(111) catalysts studied in this thesis, Zn/Pt and Ni/Pd bimetallic catalysts were studied. Preparation of these bimetallics necessitated the use of an evaporative metal source which consisted of two 0.2 mm tungsten filaments spot welded to copper power leads, onto which 0.1 mm or thinner Ni or Zn wires were tightly wrapped onto to form the metal source, as displayed in Figure 2.6. Current was passed through the power leads to resistively heat the tungsten filaments and produce a molecular flux of the Ni or Zn sources that was monitored by a quartz crystal microbalance (QCM) situated in plane with the catalyst crystal.

![Figure 2.6: Schematic of the metal deposition configuration. Tungsten filaments were used to resistively evaporate tightly coiled metal wire sources for line of sight metal deposition onto the catalyst surface while monitoring total metal deposition with an in-plane QCM.](image)

As will be discussed in greater detail in later chapters, these bimetallic catalyst surfaces could assume a variety of different surface structures based on the preparation methodology. In the case of the Ni/Pd bimetallic catalysts studied, two general bimetallic
forms were produced. The first was a Ni-Pd-Pd surface, comprised of a metastable surface monolayer of Ni on top of the Pd(111) surface, prepared by depositing 1 ML of Ni onto the Pd(111) surface while maintaining the Pd crystal at 300 K. The second surface was a Pd-Ni-Pd subsurface Ni monolayer, prepared by depositing 1 ML of Ni onto the Pd(111) surface while maintaining the Pd crystal at 600 K followed by quenching the temperature to either room temperature or cryogenic temperatures. For the Zn/Pt bimetallic catalysts, sub-monolayer quantities of Zn were dosed onto the Pt(111) surface while keeping the Pt crystal at room temperature or cooler to produce an ordered adatom overlayer. If this adatom Zn/Pt(111) surface was then annealed to 600 K for 2 minutes, a near-surface PtZn/Pt(111) alloy would form.

2.4 Temperature Programmed Desorption

One of the essential analytical tools in UHV surface science is temperature programmed desorption (TPD), also referred to as flash desorption or thermal desorption spectroscopy. TPD is a technique that was devised to investigate the kinetics of molecular desorption from well defined surfaces and identify bonding and reaction characteristics as well as quantify molecular adsorption. The general concept for performing a TPD experiment in a vacuum environment involves four main steps: (1) adsorbing a molecule of interest onto the single crystal catalyst surface, (2) linearly ramping the temperature of the crystal surface while positioned in front of a (3) quadrupole mass spectrometer that is set to monitor the major cracks of the desorption products, from which (4) the collected data can be analyzed to determine reactive, kinetic, and quantitative parameters. An
example dataset showing both zeroth and first order desorption features is displayed in Figure 2.7.

![Figure 2.7: Example TPD spectrum displaying a multilayer glycolaldehyde exposure on a Pd(111) surface, illustrating the different components of a typical TPD dataset.](image)

To better understand how to extract parameters from the data such as the activation energy for desorption, it is instructive to identify the theory behind the desorption phenomenon. To start, the rate of desorption can be given by

$$\frac{-dN}{dt} = k_d N^m$$  \hspace{1cm} (2.5)

with $N$ as the number of molecules adsorbed on the surface, $m$ is the reaction order, and $k_d$ is the desorption rate constant given by

$$k_d = Ae^{-E_d/RT}$$  \hspace{1cm} (2.6)
where $A$ is a pre-exponential factor, $E_d$ is the activation energy for desorption and $T$ is absolute temperature. Noting that the heating rate is linear in time (a constant heating rate of $dT/dt = \beta = 4$ K/s was used for all TPD experiments in this thesis), we can represent the desorption rate with respect to temperature:

$$ - \frac{dN}{dT} = - \frac{dN}{dt} \frac{dt}{dT} = N m \frac{A}{\beta} e^{-E_d/RT} $$  (2.7)

If we identify a first order desorption peak maximum at temperature $T_p$ as seen in Figure 2.7 labeled for the CO peak, we can note that the derivative of equation 2.7 at that point will be zero. Putting this all together we can come up with an expression relating $E_d$ to the first order desorption peak maximum temperature $T_p$,

$$ \frac{E_d}{RT_p^2} = \frac{A}{\beta} e^{-E_d/RT_p} $$  (2.8)

that can be solved for iteratively with the assumption that the pre-exponential factor is on the same order of magnitude as the molecular vibration frequency, estimated at $10^{-13}$ s$^{-1}$. Furthermore, analysis by Redhead$^{73}$ has shown that, under the assumption that the activation parameters are independent of surface coverage and the desorption kinetics are first order, the activation energy for desorption can be estimated by what is known as the Redhead equation:

$$ E_d = RT_p \left[ \ln \left( \frac{A}{\beta} T_p \right) - 3.64 \right] \text{ for } 10^8 < \frac{A}{\beta} < 10^{13} $$  (2.9)

In addition to using the TPD data to determine activation energies for desorption, TPD spectra can be integrated to determine initial surface coverage. This, however, requires both calibration to a known coverage of reagent, such as the saturation exposure.
of CO on the crystal surface (occupying 0.75 of Pt(111) surface atoms at saturation, for example), and subtraction of any background adsorption at the operating pressure.

2.5 High Resolution Electron Energy Loss Spectrometry

Though a rich and informative technique, TPD falls short in identifying reactive surface intermediates on the catalyst active sites, which instead requires a surface sensitive vibrational spectroscopy, namely high resolution electron energy loss spectroscopy (HREELS). HREELS operates under the principle that molecular vibrations (and wags, torsions, deformations, rocking, etc.) excite in quantized energies characteristic of their molecular composition and bonding configuration, and therefore surface bound intermediates can be identified based on the characteristic energies of excitation exhibited in a HREEL spectrum. In particular, a monochromatic electron beam is directed at the surface of interest and, though most electrons will reflect elastically off the sample into the detector, any surface species having a dipole moment oriented perpendicular to the surface can vibrationally excite, resulting in a quantized loss of energy in the electron that is manifested as a peak in the energy loss spectrum. A cartoon schematic of the HREELS operating principle is displayed below in Figure 2.8.

In all the studies carried out within this thesis, HREEL spectroscopy was performed operating with a 4 eV collimated electron beam that was tuned to produce an elastic peak of 100,000 – 1,000,000 counts per second at a full width half maximum (FWHM) of 5 meV or less. Throughout this thesis, HREELS energies are often reported in wavenumbers (cm\(^{-1}\)), where 1 meV = 8.065 cm\(^{-1}\). Additionally, all scans were taken in the specular direction at 60° with respect to the surface normal. Procedurally, the
instrument was tuned to optimal monochromator and lens element settings on a clean
catalyst surface prior to dosing the feed molecule of interest, after which a short period of
additional tuning was sometimes required to maintain resolution and count rate. To
prevent kinetic phenomena from occurring while data was collected, the sample was
maintained at cryogenic temperatures during all HREELS scans. In order to identify the
thermal evolution of surface and reaction intermediates, the sample would be flashed to
sequentially higher temperatures and quenched back to cryogenic temperatures in
between HREELS scans, resulting in a temperature sequence spectrum.

Figure 2.8: Cartoon schematic of HREEL spectroscopic principle where the mono-energetic
collimated electron beam at energy \( \varepsilon \) can either (a) reflect elastically at no loss of energy, resulting in
detection at 0 energy loss forming the (b) elastic peak in the HREEL spectrum, or (c) interact with a
surface species dipole, exciting the molecular vibration to the next energy level at \( \delta \) above the ground
state, resulting in a reflected electron that is detected at \( \varepsilon - \delta \) energy, showing up as (d) a peak in the
HREEL spectrum at \( \delta \) energy loss.
It is worth noting some of the limitations of the HREELS technique, particularly when adsorbing larger or functionally complex molecules. First off, as indicated above, vibrational excitations occur through interaction of the incident electron with the adsorbate dipole, and thus the intensity of the excitation (and corresponding energy loss peak) is a function of both the strength of the molecular dipole and its orientation with respect to the surface. Orientation plays a large role in this so termed “surface selection rule” due to the fact that perpendicular molecular dipoles are reinforced by induced image dipoles in the metal surface and parallel molecular dipoles are damped out by the corresponding induced image dipole, as illustrated in Figure 2.9. This results in an inability to use HREELS peak intensities to identify relative quantities of functional features in the surface intermediate. Furthermore, as molecules become more functionally complex, multiple excitations may overlap within the same energy loss range, making it difficult to deconvolve vibrational features, particularly when there are multiple
instances of similar functions (i.e. having more than one secondary alcohol in a glucose molecule). With this being said, careful use of model compounds and corroborative analysis with TPD data can make HREELS a powerful tool in identifying surface and reactive intermediates partaking in a catalytic reaction.

### 2.6 Auger Electron Spectroscopy

Probing the chemical composition of a catalyst surface is an important part of performing surface science studies, particularly when the surface is catalytically active for carbon coke formation, where identifying the cleanliness of the surface before a reaction becomes essential. One technique ideal for this niche is Auger electron spectroscopy, or AES. This surface science technique takes advantage of atom-specific Auger electrons originating from the autoionization phenomenon known as the Auger effect. The Auger effect, as illustrated by Figure 2.10, is initiated by a collision between a high-energy electron from the electron beam source (typically 1 – 10 keV) and an atomic core electron on the substrate. This collision results in the emission of the core electron, leaving behind a core hole. At this point, the atom will undergo a relaxation whereby an electron of lower binding energy (known as the “down” electron) will transition into the core hole to fill the vacancy, releasing an element-specific quantum of energy. This quantum of energy can either be emitted as a photon, or, in the case of the Auger effect, it can be transmitted to a third electron of even lower binding energy, known as the Auger electron, causing it to be emitted with an element-specific quantity of kinetic energy. Ultimately, the Auger effect will leave two electron vacancies in the participating atom. One of the features that make Auger electron spectroscopy so versatile is the fact that, as
noted above, the Auger electrons are emitted with element-specific kinetic energies, independent of the energy of the incident electron from the e-beam, making it possible to identify the composition of the substrate surface.

Figure 2.10: Schematic representation of the Auger effect. An incident electron from the e-beam source collides with an atomic core electron resulting in an initial electron photoemission and the leaving of a core electron vacancy. To fill the vacancy, an electron of lower binding energy (the “down” electron) will transition to the core vacancy, emitting a quantum of energy sufficient to photoemit an electron of even lower binding energy, which is known as the Auger electron.

In surface science studies, AES is often used to check a catalyst surface for carbon impurities. Graphitic carbon buildup on a catalyst surface can substantially decrease catalyst activity, and so AES can be used to confirm that a catalyst surface is sufficiently “clean” of carbon before performing any subsequent analyses. This is done by comparing the carbon Auger signal to the Auger signal of the catalyst metal. It is important to note, however, that when bombarding a surface with a high energy electron beam, a considerable amount of secondary emissions occur, these being electrons that have undergone multiple energy losses by excitation or interband transitions. This is manifested as a large, sloping background peak in the detector signal, making it difficult to interpret the superimposed Auger peaks. To circumvent this, it is customary to
represent an Auger spectrum as the differentiated signal, as is shown in the example spectrum for a Mo(100) surface in Figure 2.11. It can be shown that the “peak to peak” height of an Auger feature in the derivative space is proportional to the surface concentration of that respective element, allowing it to be used for comparative quantification. An example of a peak to peak measurement is illustrated in Figure 2.11.

Figure 2.11: Example Auger spectrum for a Mo(100) single crystal, showing the increase of carbon content after treatment with ethylene. To quantitatively demonstrate carbon deposition, peak-to-peak ratios of ● C(271 eV) and ▲ Mo(186 eV) Auger peaks are displayed to the right of the spectrum.

Summary

Molecules derived from cellulosic biomass, such as glucose, represent an important renewable feedstock for the production of hydrogen and hydrocarbon-based fuels and chemicals. Development of efficient catalysts for their reformation into useful products is needed; however, this requires a detailed understanding of their adsorption and reaction on catalytically active transition metal surfaces. In this paper we demonstrate that the standard surface science techniques routinely used to characterize the reaction of small molecules on metals are also amenable for use in studying the adsorption and reaction of complex biomass-derivatives on single crystal metal surfaces. In particular, Temperature Programmed Desorption (TPD) and High Resolution Electron Energy Loss Spectroscopy (HREELS) combined with Density Functional Theory (DFT) calculations were used to elucidate the adsorption configuration of D-glucose and glycolaldehyde on Pt(111). Both molecules were found to adsorb in an $\eta_1$ aldehyde configuration partially validating the use of simple, functionally-equivalent model compounds for surface studies of cellulosic oxygenates.

3.1 Introduction

While the utilization of H\textsubscript{2} in “clean” fuel cells is often touted as a green energy conversion technology, reforming of carbonaceous fossil fuels, such as CH\textsubscript{4}, is responsible for 96% of global H\textsubscript{2} production\textsuperscript{14}. Although this approach may have efficiency advantages over burning these fuels directly, it results in net CO\textsubscript{2} emissions and has a considerable carbon footprint. The goal of a clean energy conversion technology based on H\textsubscript{2} is thus contingent on the development of a carbon neutral means of H\textsubscript{2} production\textsuperscript{76}. As outlined in Chapter 1, catalytic aqueous phase reforming of biomass-derived sugars (e.g. glucose) using noble metal catalysts is one route for achieving this goal\textsuperscript{29,77}. A detailed understanding of the catalytic pathways involved in this process is needed, however, for this technology to be fully developed. Unfortunately, it is generally thought that the complexity of C\textsubscript{6} cellulosic oxygenates along with their low vapor pressures precludes the use of ultra-high vacuum (UHV) surface analysis methods that have been so successful in mapping out the energetics and pathways of surface-catalyzed reactions of simpler molecules\textsuperscript{78,79}. Herein we show that this is not the case and demonstrate the successful use of UHV techniques, temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS), coupled with density functional theory (DFT) to determine the bonding configuration of D-glucose on the Pt(111) surface and products of its decomposition. Furthermore, similarities in the surface bonding of glycolaldehyde (HOCH\textsubscript{2}-CH=O), the smallest model compound containing the primary functional groups in glucose, demonstrates the
validity of using this molecule as a surrogate in studies of the reaction pathways of sugars on catalytic surfaces.

3.2 Results and Discussion

The low vapor pressure of solid D-glucose prevents its introduction into the UHV environment using conventional leak valve methodology; therefore, in this study D-glucose was introduced into the system using an effusion source consisting of a resistively heated quartz tube filled with solid D-glucose (Sigma Aldrich, 99.5% pure), as described in Chapter 2. The low stability and high vapor pressure of glucose at the chamber bakeout temperature required that the quartz tube be housed in a high-vacuum (~5x10^{-9} torr) side chamber that was isolated by a gate valve from the main UHV system (maintained at 2x10^{-10} torr base pressure). This experimental setup is shown schematically in Figure 2.5. Controlled molecular deposition of D-glucose onto the atomically clean Pt(111) surface was performed by heating the effusion cell to a temperature (typically 400 K) sufficient to obtain a reproducible flux of glucose molecules while remaining below the temperature marking the onset of thermal decomposition of glucose, 438 K.67,80 This was followed by opening of the gate valve to allow this flux to impinge on the Pt(111) surface for a controlled time. Glucose exposures were measured in Torr-seconds based on ion gauge pressure measurements from the background of the chamber, though it should be noted that they may not be respective of the local pressure in the molecular beam.

The flux from the effusion source was verified by mass spectrometry (UTI quadrupole) to be D-glucose rather than smaller molecular fragments. This is
demonstrated by the TPD data for M/e = 73, a characteristic mass fragment for D-glucose, displayed in Figure 3.1a. This spectrum was obtained following a 5x10\(^{-6}\) Torr-seconds D-glucose exposure producing a multilayer coverage on the Pt(111) crystal held at 120 K. The spectrum contains a narrow peak at 357 K, whose shape is indicative of zero-order desorption kinetics, which is typical for physisorbed multilayers on metal surfaces. The assignment of this peak to D-glucose was further confirmed by the appearance of identical peaks at M/e values for the other primary glucose cracking fragments (M/e = 31, 43, 57, 60, 61, 71) with the expected relative intensities as reported in the NIST mass spectrometry database.

Figure 3.1: TPD spectra following a 5x10\(^{-6}\) torr-second D-glucose exposure on Pt(111) for (a) main glucose crack (M/e = 73) and (b) H\(_2\) (M/e = 2) and CO (M/e = 28).
CO and H$_2$ were the only reaction products detected during TPD from the glucose-dosed Pt(111) surface, resulting from reaction of chemisorbed glucose in the first monolayer. The CO and H$_2$ desorption spectrum from the multilayer glucose coverage is displayed in Figure 3.1b. Both H$_2$ and CO were found to desorb in broad peaks centered at 404 K. It is noteworthy that the molecular surrogate glycolaldehyde reacted similarly on Pt(111) to form exclusively CO and H$_2$, as shown in Figure 3.2, although there was some variance in the peak shapes and positions relative to those for glucose.

![Figure 3.2: TPD spectra following a 1 L glycolaldehyde exposure on Pt(111) for (a) main glycolaldehyde crack (M/e = 60) and (b) H$_2$ (M/e = 2) and CO (M/e = 28).](image)

Commonalities in the adsorbate-surface interactions for D-glucose and glycolaldehyde on Pt(111) were investigated using DFT methods and the most
probable adsorption configurations were predicted. Calculations were performed using the SIESTA code\textsuperscript{85, 86} employing Troullier-Martins norm-conserving scalar relativistic pseudopotentials,\textsuperscript{87} a double zeta plus polarization basis set, and the Perdew-Burke-Ernzerhof form of the generalized gradient approximation functional.\textsuperscript{88} A 4 layered, 4x4 unit cell was used to avoid periodic interactions of the larger adsorbate (a 3x3 unit cell was used for glycolaldehyde) and the surface Monkhorst Pack meshes of 3x3x1 k-point sampling was used. The bottom two layers were fixed at the bulk Pt-Pt distance while the top two layers were allowed to relax. An energy shift of 0.01 eV determined the localization radii of the basis functions. The calculations were performed at a fixed surface concentration, which inhibits intermolecular hydrogen bonding that might be present in the experiments. It is worth noting that the HREELS results shown below indicated the presence of an aldehyde moiety when adsorbing glucose, thus motivating calculations of the open-chain isomer of glucose.

Figure 3.3: Bonding configurations for glycolaldehyde and glucose on Pt(111) as determined by DFT. Pt, C, O and H atoms are represented by gray, black, red and white circles, respectively. Insets show top views. Only the most stable configurations of (A) $\eta_2\mu_2$(O,O) glycolaldehyde; (B) $\eta_3\mu_3$(O,C,O) glycolaldehyde; (C) $\eta_1\mu_1$(O) D-glucose; and (D) $\eta_2\mu_2$(C,O) D-glucose are included.
The DFT calculations indicate that glycolaldehyde adsorbs via the two stable configurations shown schematically in Figure 3.3 A and B. The \( \eta_3\mu_3(O,C,O) \) configuration (\( \eta_2\mu_2(O,C) \) adsorption of the aldehyde function) is approximately 0.4 eV more stable than the \( \eta_2\mu_2(O,O) \) configuration (\( \eta_1\mu_1(O) \) adsorption of the aldehyde function). This trend is typical of aldehydes where the weaker binding mode consists primarily of an interaction between the oxygen lone pair orbital and the metal.\(^{29}\) Geometrically, the \( \eta_3\mu_3(O,C,O) \) adsorption configuration results in the carbonyl C-O bond being parallel to the surface, whereas the aldehyde C-O bond in the weaker \( \eta_2\mu_2(O,O) \) binding is more perpendicular to the surface. The DFT results show that the major difference in the calculated vibrational spectra between the two stable binding configurations is the frequency of the \( \nu(CO) \) stretching mode of the carbonyl group at 1703 cm\(^{-1}\) in the \( \eta_2\mu_2(O,O) \) species and 978 cm\(^{-1}\) in the \( \eta_3\mu_3(O,C,O) \) species (see Table 3.1).

<table>
<thead>
<tr>
<th>Binding Mode</th>
<th>( Q ) / eV</th>
<th>( \nu(CO) ) / cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{Glycolaldehyde}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas-phase</td>
<td>-</td>
<td>1741</td>
</tr>
<tr>
<td>( \eta_2\mu_2(O,O) )</td>
<td>-0.26</td>
<td>1703</td>
</tr>
<tr>
<td>( \eta_3\mu_3(C,O,O) )</td>
<td>-0.65</td>
<td>978</td>
</tr>
<tr>
<td>\textbf{D-Glucose}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas-phase</td>
<td>-</td>
<td>1735</td>
</tr>
<tr>
<td>( \eta_1\mu_1(O) )</td>
<td>-0.21</td>
<td>1654</td>
</tr>
<tr>
<td>( \eta_2\mu_2(C,O) )</td>
<td>-0.50</td>
<td>1080</td>
</tr>
</tbody>
</table>

Similar trends are observed for the adsorption of D-Glucose on Pt(111). The \( \eta_2\mu_2(C,O) \) adsorption mode is approximately 0.3 eV more stable than the \( \eta_1\mu_1(O) \) adsorption mode. Interactions among hydroxyl functions in D-glucose result in
intramolecular stabilization. These interactions cause the upright configurations (Figure 3.3 C and D) to have lower energies than corresponding configurations with hydroxyl-metal interactions which disturb intramolecular hydroxyl interactions. Similar to glycolaldehyde, the ν(CO) mode of the carbonyl group appears at 1654 cm⁻¹ for the η₁μ₁(O) species and shifts to 1080 cm⁻¹ for the η₂μ₂(C,O) binding mode.

The predicted ν(CO) frequencies can be used in conjunction with HREELS vibrational spectra of the adsorbed glycolaldehyde and D-glucose intermediates to determine their bonding configuration on Pt(111). The HREEL spectrum of the glycolaldehyde-dosed surface at 150 K in Figure 3.4 shows that the C-O stretching region is dominated by a peak at 1718 cm⁻¹, which is consistent with that in the free molecule (see Table 3.1) indicating a weakly physisorbed species. Upon heating to 250 K this peak shifts to 1666 cm⁻¹ suggesting the formation of the η₂μ₂(O,O) intermediate. Note that even at higher temperatures, the HREELS results do not provide strong evidence for the formation of the di-σ bonded η₃μ₃(O,C,O) intermediate as predicted by DFT. Given the relatively small difference in the energies of the two configurations, this discrepancy may be due to steric interactions between adjacent adsorbates or reduction of back-donation to the carbonyl group, resulting from electronegative surface agents.⁸⁹
Figure 3.4: HREELS temperature sequence obtained from Pt(111) following a 1 L glycolaldehyde dose.

Similar to glycolaldehyde, the HREEL spectra of D-glucose in Figure 3.5 contain a C-O stretching peak at 1666 cm\(^{-1}\) at low temperatures. This corresponds to the DFT-predicted $\eta_1\mu_1$(O) bonding configuration for glucose (Figure 3.3C) which is analogous to the $\eta_2\mu_2$(O,O) glycolaldehyde species. Note that upon heating to 355 K this peak shifts to 1627 cm\(^{-1}\), but this may be a result of partial catalytic decomposition of the glucose as indicated by the onset of the $\nu$(C=O) modes for adsorbed CO at 1799 and 2045 cm\(^{-1}\), which is further corroborated by the onset of desorption of the CO product in TPD (Figure 3.1).
Figure 3.5: HREELS temperature sequence obtained from Pt(111) following a 5x10^{-6} torr-second D-glucose dose.

Of additional interest is the disappearance of the broad OH stretch at ~3400 cm\(^{-1}\) after heating to 300 K for glycoaldehyde and 355 K for glucose, indicative of O-H bond cleavage. Emergence of linear and bridge bonded CO in both samples after heating above 350 K, as indicated by peaks at 2045 and 1799 cm\(^{-1}\), respectively, corresponds to the production of CO via molecular decomposition. This is complimented by the disappearance of the intense vibrational peaks at 620 cm\(^{-1}\) and 1050 cm\(^{-1}\) corresponding to \(\delta(CCO)\) and \(\nu(CO)\) vibrations of the intact molecule\(^{37, 90}\), respectively, which corroborates C-C scission and formation of CO. The linear and bridge bonded CO peaks
are not evident at 450 K as this temperature is beyond the desorption temperature of CO on Pt(111).

3.3 Conclusions

In conclusion, the experimental implementation of a low vapor pressure cellulosic oxygenate, D-glucose, in a UHV surface science study was achieved, demonstrating the feasibility of using a battery of UHV surface science techniques for future studies to determine the reaction pathways of C₆ sugars on model catalytic surfaces. Equally important, strong similarities were observed between the adsorption and reaction of D-glucose and the model compound glycolaldehyde. In particular, both oxygenates were found to bond to the surface via the carbonyl group in an η₁ configuration, undergo O-H bond cleavage between 250 and 355 K, and decompose above 355 K to produce CO and H₂. This study not only sets the stage for using C₆ cellulosic oxygenates in fundamental surface science experiments, but also validates the use of functional group surrogates, such as glycolaldehyde, to help in unraveling the complex surface chemistry of these species.
Chapter 4. Correlating the Surface Chemistry of C₂ and C₃ Aldoses with a C₆ Sugar: Reaction of Glucose, Glyceraldehyde and Glycolaldehyde on Pd(111)*

Summary

The catalytic conversion of biomass into fuels and chemicals requires an understanding of the adsorption and reaction of C₅ and C₆ sugars on catalytically active metals. In this investigation glycolaldehyde and glyceraldehyde were used as model compounds in a density functional theory (DFT) and experimental surface science study of the reaction of sugars on Pd(111). For the first time the stable intermediates formed by glucose on a single crystal metal surface were identified allowing for comparisons with the surrogate molecules. Adsorption was governed by aldehyde group-surface interactions forming \( \eta_1(C=O) \) intermediates, which, upon heating, transformed into more stable \( \text{di-}\sigma \eta_2(C-O) \) species followed by \( \alpha\)-O-H bond scission to produce an \( \alpha\)-oxo-\( \eta_2 \) intermediate. A consequence of the surface-carbonyl group interaction is that it precludes using simple alcohols or polyols as model compounds for biomass-derived sugars in mechanistic studies of heterogeneously catalyzed biomass reforming on metal surfaces and suggests that simple aldoses are more appropriate surrogates.

4.1 Introduction

As explained in Chapter 1, environmental maladies associated with fossil fuels have motivated the use of biomass-derived molecules as potentially carbon-neutral, alternative feedstocks for the production of fuels and chemicals. This has prompted research into catalytic routes for reforming of the building blocks of biomass, C$_5$ and C$_6$ sugars such as xylose and glucose.$^{24, 28, 91}$ These are polyols in which the carbon atoms are functionalized with hydroxyl groups. In their cyclic isomer forms the ring is closed by an ether linkage, which is converted to an aldehyde group in the open chain isomer as shown in Figure 4.1. The oxygenated character of these molecules presents challenges for the production of fuels and chemicals: reforming to hydrogen requires selective C-H and O-H bond scission, while production of fuels and chemicals requires at least partial de-oxygenation, for which selective C-O bond scission is required.

![Figure 4.1: (a) Closed ring and (b) open chain forms of glucose.](image)

Group 10 transition metals are often used as catalysts for the transformation of biomass-derived oxygenates into useful products,$^{92}$ and numerous fundamental studies of the reaction of simple and multifunctional oxygenates on model single crystal surfaces of these metals have appeared in the literature.$^{37, 40, 42, 46}$ Several recent reviews provide an overview of this work.$^{93, 94}$ The majority of these surface science studies have relied on
using small molecular surrogates, such as ethanol or ethylene glycol, rather than the sugars themselves to investigate relevant reaction pathways. This simplified approach facilitates the use of standard surface sensitive spectroscopic probes, such as temperature-programmed desorption (TPD), x-ray photoelectron spectroscopy (XPS) and high-resolution electron energy loss spectroscopy (HREELS), and has provided some insights into how multifunctionality affects the energetics of the surface reactions. For example, a recent study on the reaction of ethylene glycol (HOCH$_2$CH$_2$OH) on Pt(111)$^{95}$ found that the C-H bond scission barrier in adsorbed ethylene glycol was higher than that for O-H scission causing the molecule to decompose through initial O-H bond scission to form an HOCH$_2$CH$_2$O alkoxide intermediate. This is in contrast to monoalcohols where initial C-H scission has a lower energy barrier. This energetic difference can be explained by the initial adsorption configuration for ethylene glycol where interaction of the oxygens with the surface produces a bidentate complex where the C-O bonds are more perpendicular to the surface compared to those in the monoalcohols. This results in close proximity of the hydroxyl hydrogens to the surface and minimizes the interaction of the $\alpha$-hydrogens with the surface.

While this example illustrates the insights that can be obtained in studies of the adsorption of simple molecular surrogates for sugars on metals, whether these insights are transferable to the surface chemistry of more complex sugars is an open question. Herein we have addressed this issue using TPD and HREELS in conjunction with density functional theory (DFT) calculations to investigate the adsorption and reaction of a series of multifunctional aldoses (i.e. oxygenates that contain one or more OH groups and a
single aldehyde group) on Pd(111). In particular, the specific molecules that were investigated included glycolaldehyde (C$_2$H$_4$O$_2$), glyceraldehyde (C$_3$H$_6$O$_3$), and glucose (C$_6$H$_{12}$O$_6$). As will be discussed below, these molecules are all solids at room temperature which complicates their introduction into an ultra-high vacuum (UHV) surface analysis chamber and necessitates the use of a molecular beam dosing system. The results obtained in this study allowed both the initial adsorption configurations of the aldoses on Pd(111) and the stable adsorbed intermediates that form via reaction of these molecules at higher temperatures to be elucidated. This investigation demonstrates that fundamental surface science studies of the reaction of complex aldoses on model catalytic surfaces are tractable and, to our knowledge, it provides the first example of a detailed experimental and theoretical study where both the adsorption configuration of glucose and the stable surface intermediates that are formed from it on a well-defined metal surface have been characterized.

### 4.2 Experimental Methods

Experiments were performed in an ultra high vacuum (UHV) chamber with a 2×10$^{-10}$ Torr background pressure, described in great detail within Chapter 2. Auxiliary to the main UHV apparatus was a smaller chamber connected to the main chamber via gate valve, containing the effusion cells used to dose glyceraldehyde and glucose into the main chamber.

The Pd(111) single crystal (10×5×1 mm, Princeton Scientific) was cleaned using repeated cycles of 2 kV Ar$^+$ sputtering for 30 min, followed by annealing in vacuum at 1100 K for 15 min, and in 2×10$^{-8}$ Torr of O$_2$ at 1100 K for 20 min. For all experimental
The data presented herein, the stated cleaning procedure was used before any substrate was dosed. The sample was heated resistively and cooled to 100 K via conduction from an N\textsubscript{2} reservoir. A 4 K/s heating rate was used in all TPD experiments and HREEL spectra were collected in the specular direction using a 4 eV electron beam directed 60° with respect to the surface normal. The full width half maximum (fwhm) for the HREEL spectra elastic peak was typically 40 cm\textsuperscript{-1}.

Glycolaldehyde dimer (Pfaltz and Bauer, 98%), a crystalline solid at room temperature, was used as the glycolaldehyde source. Dissociation and sublimation of the dimers produced significant vapor pressure upon gentle heating. The source consisted of a glass bulb containing the glycolaldehyde dimer solid attached to a heated, high-vacuum dosing line connected to the UHV chamber via variable leak valve, as described in Chapter 2 and as shown in Figure 2.3. A similar method for dosing glycolaldehyde into UHV has been used previously by Yu et al.\textsuperscript{46} Mass spectrometry was used to verify that only glycolaldehyde vapors were introduced into the UHV system.

Glyceraldehyde (DL-glyceraldehyde dimer 97%, Aldrich) and glucose (D-(+)-glucose 99.5%, Sigma) are also solids at room temperature but due to their low vapor pressures could not be introduced into the UHV system in the same manner as glycolaldehyde. Instead, they were administered into the analysis chamber using molecular beams produced from micro effusion cells housed in the auxiliary vacuum chamber. A detailed description of the configuration and dosing procedure are provided in Chapter 2, with a schematic of this dosing system shown in Figure 2.5.
Heating the glyceraldehyde and glucose to 370 and 400 K, respectively, was sufficient to induce vaporization creating a molecular beam that impinged on the Pd(111) surface. When using this approach one must be careful to ensure that smaller, more volatile pyrolysis products are not produced. For glucose, differential scanning calorimetry and thermogravimetric analysis studies have shown that it does not decompose below its melting temperature of 438 K. Oja and Suuberg have measured the vapor pressure of glucose using the Knudsen effusion technique and report a vapor pressure of \(10^{-6}\) Torr at 400 K, the operating temperature of our glucose source. Production of glucose vapor in the effusion cell was also verified by the correspondence of its measured electron impact mass spectrum cracking pattern to that reported in the NIST database. For glyceraldehyde the effusion source operating temperature of 370 K is 48 K below its melting temperature. Mass spectrometry was used to verify that only glyceraldehyde vapor was produced from the effusion cell. Saturation coverages were used in all the TPD and HREELS experiments. The supplemental Section 4.6 at the end of this chapter provides a description of how the dose required to obtain saturation coverage in the first monolayer was determined for each reactant.

Density functional theory (DFT) calculations were performed using the SIESTA code. Troullier-Martins norm-conserving scalar relativistic pseudopotentials were employed, with a double zeta plus polarization (DZP) basis set. An energy shift of 0.01 eV determined the localization radii of the basis functions. A DFT supercell approach employed the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) functional. Surface Monkhorst Pack meshes of \(3\times3\times1\) k-point
sampling were used. Calculations of glycolaldehyde and glyceraldehyde used a 4 layered, 3x3 unit cell of Pd and calculations for D-glucose used a 4 layered, 4x4 unit cell to avoid periodic interactions of the larger adsorbate. The bottom two Pd layers of all energetic calculations were fixed, while the top layers and adsorbate were allowed to relax. Absolute binding energies between oxygenates of different size cannot be meaningfully compared, because dispersion corrections were not included in this study and the effective surface coverage differs between adsorbates. The procedure for calculating vibrational frequencies is described in a previous publication. It should be noted that not all possible binding configurations of glucose were explored due to the size and complexity of the molecule. The presented configurations are the most stable of the set that was explored, as guided by the DFT results for the smaller oxygenates as well as the general experimental results.

4.3 Results

Since the experimental results indicate that D-glucose, which exists most commonly in the cyclic form (Figure 4.1), undergoes ring opening upon adsorption, only the linear chain isomer of this molecule was considered by DFT. For all three molecules, two main adsorption configurations of the aldehyde function were studied: η₁(C=O), where bonding occurs via the lone pair electrons on the carbonyl oxygen, and di-σ η₂(C-O), where both the C and O in the carbonyl bond to the surface. A summary of the vibrational frequencies of these molecules is shown in Table 4.1 and schematics of the optimized adsorbate structures with adsorption energies are depicted in Figure 4.2. While absolute binding energies of the three oxygenates are dependent on interactions of hydroxyl
groups with the Pd surface and the relative stability of the gas-phase reference, \( \eta_2 \) adsorption is systematically 0.3-0.4 eV more stable than \( \eta_1 \).

The calculated vibrational frequencies for each adsorbate show that the \( \nu(C=O) \) mode in the \( \eta_1 \) configuration is shifted to a lower frequency (1649-1671 cm\(^{-1}\)) relative to that in the gas phase (1733-1741 cm\(^{-1}\)) and the \( \nu(C=O) \) mode is absent for the \( \eta_2 \) configuration. For \( \eta_2 \) glycer aldehyde and glucose, the \( \nu(O-H) \) associated with the \( \alpha \)-hydroxyl group also shifts to a lower frequency due to interactions with the Pd(111) surface and neighboring hydroxyl groups.

Initial TPD studies focused on identifying the dosage required for saturation coverage of each reactant on Pd(111) (Figure 4.6) and further verifying the production of glycer aldehyde and glucose vapors from the effusion cells used to introduce these molecules into the UHV chamber. These saturation dosages were used in the surface reactivity TPD and HREELS studies described below.
Table 4.1: DFT calculated heats of chemisorption ($Q$) and vibrational frequencies ($\nu$) of glycolaldehyde, glyceraldehyde and glucose on Pd(111)

<table>
<thead>
<tr>
<th>Species</th>
<th>Binding mode</th>
<th>$Q^*$ [eV]</th>
<th>$\nu^+$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_4$O$_2$</td>
<td>gas-phase</td>
<td>-</td>
<td>664, 746, 884, 1033, 1122, 1184, 1271, 1306, 1365, 1395, 1741, 2914, 2947, 2976, 3545</td>
</tr>
<tr>
<td></td>
<td>$\eta_1$(O)</td>
<td>-0.42</td>
<td>644, 734, 870, 996, 1099, 1177, 1252, 1290, 1354, 1374, 1671, 2925, 2958, 3031, 3524</td>
</tr>
<tr>
<td></td>
<td>$\eta_2$(C,O)</td>
<td>-0.75</td>
<td>634, 661, 770, 870, 946, 1030, 1140, 1172, 1258, 1304, 1361, 1373, 2917, 2954, 3029, 3462</td>
</tr>
<tr>
<td>C$_3$H$_6$O$_3$</td>
<td>gas-phase</td>
<td>-</td>
<td>557, 715, 806, 898, 907, 1021, 1052, 1104, 1158, 1216, 1306, 1320, 1331, 1361, 1379, 1401, 1733, 2902, 3018, 3028, 3099, 3630, 3668</td>
</tr>
<tr>
<td></td>
<td>$\eta_1$(O)</td>
<td>-0.55</td>
<td>590, 648, 801, 849, 924, 998, 1069, 1127, 1176, 1208, 1276, 1284, 1318, 1349, 1365, 1407, 1649, 2863, 2955, 3005, 3078, 3452, 3534</td>
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<td>$\eta_2$(C,O)</td>
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</tr>
<tr>
<td>C$<em>6$H$</em>{12}$O$_6$</td>
<td>gas-phase</td>
<td>-</td>
<td>555, 647, 677, 716, 765, 838, 876, 889, 925, 991, 1036, 1056, 1070, 1083, 1103, 1115, 1144, 1169, 1174, 1180, 1214, 1242, 1255, 1264, 1277, 1296, 1308, 1326, 1359, 1367, 1396, 1404, 1421, 1479, 1735, 2940, 2953, 2964, 2970, 2986, 3032, 3060, 3484, 3511, 3690, 3679, 3742</td>
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<tr>
<td></td>
<td>$\eta_1$(O)</td>
<td>-0.32</td>
<td>514, 555, 643, 659, 725, 765, 843, 878, 898, 918, 988, 1037, 1057, 1075, 1083, 1100, 1109, 1145, 1167, 1176, 1183, 1220, 1238, 1251, 1265, 1278, 1292, 1306, 1327, 1363, 1375, 1398, 1407, 1424, 1481, 1665, 2945, 2978, 2982, 2987, 3000, 3063, 3069, 3490, 3543, 3604, 3691, 3765</td>
</tr>
<tr>
<td></td>
<td>$\eta_2$(C,O)</td>
<td>-0.68</td>
<td>551, 614, 658, 726, 749, 769, 793, 865, 880, 900, 957, 1030, 1039, 1058, 1069, 1083, 1094, 1110, 1149, 1167, 1171, 1188, 1215, 1221, 1247, 1251, 1264, 1292, 1306, 1325, 1352, 1377, 1384, 1403, 1426, 1463, 2789, 2945, 2984, 2992, 3003, 3059, 3073, 3252, 3580, 3601, 3685, 3757</td>
</tr>
</tbody>
</table>

*Q not corrected for ZPE, † Only frequencies over 500 cm$^{-1}$ shown with $\nu$(C=O) stretches in bold
Figure 4.2: Schematics of DFT optimized structures for (a) \( \eta_1 \)-glycolaldehyde, (b) \( \eta_2 \)-glycolaldehyde, (c) \( \eta_1 \)-glyceraldehyde, (d) \( \eta_2 \)-glyceraldehyde, (e) \( \eta_1 \)-glucose and (f) \( \eta_2 \)-glucose on Pd(111). Carbon, hydrogen, oxygen and palladium atoms are represented by black, white, red and blue spheres, respectively. Only the top two layers of the Pd slab are shown for simplicity. Calculated energies of chemisorption, \( Q \), for each bonding configuration relative to the respective gas phase molecules are indicated below each subfigure.

Figure 4.3 displays TPD data for the gaseous products produced via reaction of each aldose on Pd(111). Note that similar behavior is observed for each molecule, with CO and H\(_2\) being the primary reaction products. For both glycolaldehyde (Figure 4.3a) and glyceraldehyde (Figure 4.3b) H\(_2\) and CO desorb between 270-277 K and 438-444 K, respectively. These peaks are desorption limited as determined by comparison to TPD data for CO- and H\(_2\)-dosed Pd(111).\(^{61, 100-103}\) Thus, the decomposition of glycolaldehyde
and glyceraldehyde on Pd(111) is facile and occurs below 270 K. Note that for glyceraldehyde, in addition to the primary CO peak at 438 K, there is a smaller shoulder at 375 K. This peak shape is typical of that for high coverages of CO on Pd(111).\textsuperscript{101} The peak at 438 K is due to desorption of CO occupying three-fold-hollow sites and the shoulder can be assigned to CO in lower coordination bridge or atop sites. Previous studies have shown that population of the lower coordination sites occurs only for high CO coverages.\textsuperscript{102, 104} The only decomposition products other than CO and H\textsubscript{2} were a small amount of CH\textsubscript{2}O at 247 K for glycolaldehyde and CH\textsubscript{3}OH at 270 K for glyceraldehyde.

Figure 4.3: Reaction TPD spectra for saturation exposures of (a) glycolaldehyde, (b) glyceraldehyde and (c) glucose on Pd(111)

For glucose (Figure 4.3c) the CO desorption peak is similar to that for glyceraldehyde, but H\textsubscript{2} desorbs at a slightly higher temperature of 323 K. This temperature is within the range reported for desorption limited H\textsubscript{2} from Pd(111), but only for low hydrogen coverages. The area of this peak, however, indicates a high hydrogen coverage suggesting that it is reaction limited. The small CO\textsubscript{2} peak at 323 K supports this
conclusion. These results suggest that glucose-derived fragments are more stable on Pd(111) relative to glycolaldehyde and glyceraldehyde.

Finally, for glyceraldehyde and glucose the CO and H₂ yield was found to decrease in sequential TPD runs. We attribute this to carbon being deposited on the surface. Unfortunately due to overlap of the C and Pd AES signals it was not possible to quantify the extent of carbon deposition using this technique.

Figure 4.4a shows the evolution of the HREEL vibrational spectrum with temperature for Pd(111) dosed with a saturation coverage of glycolaldehyde at 115 K. The peak positions are tabulated in Table 4.2 with the IR spectrum of molecular glycolaldehyde, and the HREEL spectra of glycolaldehyde on Pt(111) and propanaldehyde (CH₃CH₂CHO) on Pd(111)⁴⁶,⁹⁰ for comparison. Note that the vibrational spectrum for glycolaldehyde/Pd(111) at 115 K is similar to that of the gaseous molecule and the primary peaks can be assigned as follows: a broad \( \nu(\text{OH}) \) stretch at 3315 cm⁻¹, \( \nu(\text{C}=\text{O}) \) stretch at 1715 cm⁻¹ corresponding to the CHO group,⁴⁶,⁹⁰ a strong \( \nu(\text{CO}) \) stretch at 1057 cm⁻¹ corresponding to the hydroxyl COH group, a \( \nu(\text{CC}) \) stretch⁴⁶ at 880 cm⁻¹, and a broad \( \delta(\text{CCO}) \) deformation peak at 640 cm⁻¹. The assignment of this latter peak is consistent with that reported for propanaldehyde/Pd(111).⁹⁰

Before assigning the bonding configuration of glycolaldehyde on Pd(111) at 115 K it is useful to consider the bonding of simple alcohols and aldehydes on this surface. It is well established that alcohols adsorb dissociatively on Pd(111) to form alkoxides,³⁷,¹⁰⁵ while two bonding configurations have been observed for aldehydes, \( \eta_1(\text{C}=\text{O}) \) and di-\( \sigma \) \( \eta_2(\text{C}-\text{O}) \). Acetyl intermediates can also be formed from aldehydes via cleavage of the C-
H bond on the carbonyl carbon. The presence of a ν(OH) stretch at 3315 cm$^{-1}$ in the HREEL spectrum of glycolaldehyde/Pd(111) indicates that the OH group remains intact, and the lack of a ν(C-O) stretch near 1570 cm$^{-1}$, indicative of adsorbed acetyl intermediates, allows the formation of alkoxide and acetyl species at 115 K to be ruled out. Thus, bonding to the surface must occur via the carbonyl group. It should be noted that the ν(OH) stretch is at a lower frequency than that of the vapor phase, indicating possible intermolecular hydrogen bonding or interaction of the alcohol oxygen lone pairs with the metal surface.

The position of the ν(C=O) stretch at 1715 cm$^{-1}$ is only slightly perturbed relative to that in the gaseous molecule, indicating bonding in the η$_1$(C=O) configuration. Note, however, the possibility that some di-σ η$_2$(C-O) species are also formed cannot be ruled out since the ν(CO) stretch of this specie would overlap with the δ(CH$_2$) and γ(CH$_2$) modes at 1390 cm$^{-1}$.

Heating to 185 K caused only minor changes in the vibrational spectrum including a decrease of the peaks for the ν(OH) stretch and δ(CCO) deformation. The change in the ν(OH) stretch signifies the interaction of the OH group with the surface and the onset of OH bond scission. The resulting constraint of the molecular backbone may be responsible for the change in the δ(CCO) deformation. More significant changes occurred upon heating to 200 K, including a decrease in intensity of the η$_1$ ν(C=O) peak at 1715 cm$^{-1}$, a shift of ν(C-H) from 2827 to 2980 cm$^{-1}$, and the emergence of a ν(Pd-C) stretch at 269 cm$^{-1}$. These changes point to a shift from an η$_1$(C=O) aldehyde adsorption configuration to an η$_2$(C-O) configuration where both the carbonyl oxygen and carbon are bonded to
the surface. The \( \nu(C-O) \) stretch of an \( \eta_2 \) species adsorbed on Pd(111) has been reported to occur between 1390 and 1435 cm\(^{-1} \) for simple aldehydes\(^{90} \) however, due to the dipole

![Figure 4.4: HREELS temperature series for saturation exposures of (a) glycolaldehyde, (b) glyceraldehyde, and (c) glucose on Pd(111).](image)

Table 4.2: Vibrational mode assignments for glycolaldehyde and related oxygenates

<table>
<thead>
<tr>
<th>mode</th>
<th>( \nu(OH) )</th>
<th>( \nu(CH_2, \gamma(CH) )</th>
<th>( \eta_1-\nu(C=O) )</th>
<th>( \delta(CH_2, \gamma(CH_2) )</th>
<th>( \eta_2-\nu(C-O) )</th>
<th>( \nu(C-OH) )</th>
<th>( \nu(CC) )</th>
<th>( \delta(CCO) )</th>
<th>( \nu(M-C) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu(OH) )</td>
<td>3315</td>
<td>-</td>
<td>3450</td>
<td>3549</td>
<td>-</td>
<td>1057</td>
<td>880</td>
<td>639</td>
<td>-</td>
</tr>
<tr>
<td>( \nu(CH_2, \gamma(CH) )</td>
<td>2827</td>
<td>2900, 2980</td>
<td>2875</td>
<td>2881, 2820</td>
<td>2950</td>
<td>1057</td>
<td>880</td>
<td>639</td>
<td>269</td>
</tr>
<tr>
<td>( \eta_1-\nu(C=O) )</td>
<td>1715</td>
<td>1715</td>
<td>1718</td>
<td>1754</td>
<td>1710</td>
<td>1390</td>
<td>-</td>
<td>-</td>
<td>1400</td>
</tr>
<tr>
<td>( \delta(CH_2, \gamma(CH_2) )</td>
<td>1390</td>
<td>1390</td>
<td>1394</td>
<td>1425, 1378, 1356</td>
<td>-</td>
<td>1390</td>
<td>-</td>
<td>-</td>
<td>1400</td>
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<tr>
<td>( \eta_2-\nu(C-O) )</td>
<td>-</td>
<td>1390</td>
<td>-</td>
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<td>1390</td>
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<td>1400</td>
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<tr>
<td>( \nu(C-OH) )</td>
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<td>1089</td>
<td>1112</td>
<td>-</td>
<td>1057</td>
<td>880</td>
<td>639</td>
<td>-</td>
</tr>
<tr>
<td>( \nu(CC) )</td>
<td>880</td>
<td>-</td>
<td>852</td>
<td>859</td>
<td>920</td>
<td>-</td>
<td>880</td>
<td>639</td>
<td>-</td>
</tr>
<tr>
<td>( \delta(CCO) )</td>
<td>639</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>880</td>
<td>-</td>
<td>680</td>
</tr>
<tr>
<td>( \nu(M-C) )</td>
<td>-</td>
<td>269</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>269</td>
<td>-</td>
<td>-</td>
<td>350</td>
</tr>
</tbody>
</table>

\(^{a}\)This work, \(^{b}\)Reference 46, \(^{c}\)Reference 106, \(^{d}\)Reference 90
selection rules this peak is quite small and for glycolaldehyde would be obscured by the stronger $\delta$(CH$_2$) and $\gamma$(CH$_2$) losses. This is also consistent with DFT calculations (Table 4.1) that predict the absence of a $\nu$(C=O) mode for the $\eta_2$ configuration.

![Chemical Structures](image)

**Figure 4.5:** Proposed reaction pathway for aldoses on Pd(111), with initial (a) $\eta_1$(C=O) adsorption followed by transition into a (b) $\eta_2$(C-O) configuration. O-H scission at the $\alpha$ position in the $\eta_2$(C-O) species results in the formation an $\alpha$-oxo-$\eta_2$ intermediate. The $\alpha$-oxo-$\eta_2$ species are shown for (c) glycolaldehyde, (d) glyceraldehyde and (e) glucose.

Additional changes for the 200 K spectrum include the disappearance of the $\nu$(OH) stretch at 3315 cm$^{-1}$ and the $\delta$(CCO) deformation mode at 639 cm$^{-1}$. As noted above, these changes correspond to O-H scission and the formation of a Pd-O bond suggesting the formation of an $\alpha$-oxo-$\eta_2$ surface intermediate as shown in Figure 4.5c.

Other notable features include the emergence of $\nu$(CO) stretches at 1846 and 2057 cm$^{-1}$ which are consistent with CO adsorbed in three-fold-hollow and atop sites on Pd(111),$^{102, 104}$ respectively. The production of CO is a consequence of the onset of C-C and C-H scission in the surface intermediates which is also consistent with the decrease in intensity of the $\nu$(CC) stretch at 880 cm$^{-1}$ and the $\delta$(CCO) deformation at 639 cm$^{-1}$. While on Pd(111) the formation of atop-site CO is normally preceded by the saturation of
the three-fold-hollow sites, many of these sites are likely to be blocked by the glycolaldehyde-derived surface intermediates, thereby forcing some of the CO to the less-stable atop sites. The adsorbed H resulting from C-H scission would be expected to produce a peak between 500 to 800 cm$^{-1}$; however, because the Pd-H bond has a relatively small dipole moment, the cross section for exciting this vibration is small and this peak is likely obscured by the stronger features of the organic moiety.

By 250 K, the HREELS spectrum is dominated by the CO stretch at 1846 cm$^{-1}$, consistent with continued C-C and C-H scission. Retention of the peaks at 1390 and 1057 cm$^{-1}$, however, indicates that decomposition to CO and H is not complete. Also note the emergence of a peak at 915 cm$^{-1}$, which in conjunction with the peaks at 1057 and 1390 cm$^{-1}$, can be assigned to a surface ethylidyne intermediate ($\equiv$C-CH$_3$). This suggests that some C-O bond cleavage may also occur.

Decomposition of the glycolaldehyde is nearly complete by 300 K. The HREEL spectra at 300 and 400 K contain a strong $\nu$(CO) stretch for CO adsorbed on three-fold-hollow sites, a weak $\nu$(CO) stretch for atop CO and the corresponding $\nu$(Pd-C) stretch at 269 cm$^{-1}$. The emergence of an intense peak at 755 cm$^{-1}$, the disappearance of the peak at 915 cm$^{-1}$, and a broadening of the peak at 1390 cm$^{-1}$ occur in this temperature range. The 755 cm$^{-1}$ peak can be attributed to the out of plane $\gamma$(CCH) wag of an acetylide species (-C=CH) with the broad 1390 cm$^{-1}$ peak corresponding to the associated $\nu$(CC) stretch, consistent with the literature. Ethylidyne species on Pd(111) undergo dehydrogenation to acetylide above 300 K, so the observation of adsorbed acetylide provides additional support for the ethylidyne peak assignments at 250 K.
Table 4.3: Vibrational mode assignments for glyceraldehyde and D-glucose.

<table>
<thead>
<tr>
<th>mode</th>
<th>frequency, cm$^{-1}$</th>
<th>C$_3$H$_6$O$_3$</th>
<th>C$_3$H$_6$O$_3$</th>
<th>C$_3$H$_6$O$_3$</th>
<th>C$_6$H$_12$O$_6$</th>
<th>C$_6$H$_12$O$_6$</th>
<th>C$_6$H$_12$O$_6$</th>
<th>C$_6$H$_12$O$_6$</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Pd(111) 115K</td>
<td>Pd(111) 230K</td>
<td>vapor</td>
<td>Pd(111) 115 K</td>
<td>Pd(111) 290 K</td>
<td>solid</td>
<td>vapor</td>
</tr>
<tr>
<td>ν(OH)</td>
<td>3323</td>
<td>3323</td>
<td>3386, 3128</td>
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<td>2858</td>
<td>2942*</td>
<td>2876</td>
<td>2900</td>
<td>2944</td>
<td>2998</td>
<td></td>
</tr>
<tr>
<td>ν(CH)</td>
<td>2858</td>
<td>2858</td>
<td>-</td>
<td>2900</td>
<td>2900</td>
<td>2913, 2944</td>
<td>2915,</td>
<td></td>
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<tr>
<td>η$_1$-ν(C=O)</td>
<td>1715</td>
<td>1715</td>
<td>1735</td>
<td>1715</td>
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<td>δ(CH$_2$)</td>
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<td>1453*</td>
<td>1329</td>
<td>1329</td>
<td>1460</td>
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<tr>
<td>γ(CH$_2$)</td>
<td>1357</td>
<td>1357</td>
<td>1378*</td>
<td>1443</td>
<td>1443</td>
<td>-</td>
<td>1397</td>
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</tr>
<tr>
<td>η$_2$-ν(C-O)</td>
<td>1428</td>
<td>1428</td>
<td>-</td>
<td>1443</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
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<tr>
<td>2º-ν(C-OH)</td>
<td>1076</td>
<td>-</td>
<td>1139*, 1073*</td>
<td>1079</td>
<td>1060</td>
<td>1111, 1050</td>
<td>1093, 1077</td>
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<td>1º-ν(C-OH)</td>
<td>1045</td>
<td>1057</td>
<td>1048*</td>
<td>1055</td>
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<td>ν(CC)</td>
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<td>-</td>
<td>912*</td>
<td>904</td>
<td>-</td>
<td>995</td>
<td>900</td>
<td></td>
</tr>
<tr>
<td>ν(CCC)</td>
<td>803</td>
<td>-</td>
<td>791*</td>
<td>803</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>δ(CCO)</td>
<td>675, 630</td>
<td>630</td>
<td>656*</td>
<td>632</td>
<td>-</td>
<td>776</td>
<td>626</td>
<td></td>
</tr>
<tr>
<td>ν(M-C)</td>
<td>278</td>
<td>278</td>
<td>-</td>
<td>-</td>
<td>302</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

*aThis work, ^aReference$^{112}$, ^bReference$^{113}$, ^cReference$^{114}$, ^dNot assigned in Reference$^{112}$.

A similar HREELS data set for a saturation exposure of glyceraldehyde/Pd(111) is presented in Figure 4.4b with peak assignments given in Table 4.3. At 115 K notable features include a strong ν(C=O) stretch at 1715 cm$^{-1}$, a broad ν(OH) stretch at 3323 cm$^{-1}$ and two ν(CO) stretches at 1045 and 1076 cm$^{-1}$. Since the ν(CO) stretch for secondary alcohols occur at slightly higher frequencies than that for primary alcohols, the ν(CO) stretches at 1045 and 1076 cm$^{-1}$ are, therefore, assigned to the primary and secondary C-OH groups, respectively. The detection of a relatively intense ν(C=O) peak at 1715 cm$^{-1}$ whose frequency is only slightly lower than that in the gaseous molecule, as well as the
ν(OH) and ν(C-OH) stretches marking intact hydroxyl groups indicates adsorption primarily in the η₁ aldehyde configuration. Relatively few changes are apparent upon heating to 180 K, indicating that the η₁ bonding configuration persists at this temperature. Consistent with the glycolaldehyde results, significant changes were observed upon heating the glyceraldehyde/Pd(111) surface to 230 K. These include a decrease in the intensity of the ν(C=O) peak at 1715 cm⁻¹ and a large increase in the intensity of the ν(Pd-C) peak at 278 cm⁻¹. These changes can be attributed to a transformation from the η₁ to the η₂ aldehyde configuration. This conclusion is consistent with the DFT calculations (Table 4.1) which predict that the η₂ configuration is more energetically favorable. Additional significant changes in the spectrum include disappearance of the ν(CCC) bend at 803 cm⁻¹ and the ν(CO) stretch at 1076 cm⁻¹.

As noted above for glycolaldehyde, scission of the O-H bond upon heating to 200 K, as signified by the disappearance of the ν(OH) stretch 3315 cm⁻¹, resulted in the formation of an α-oxo-η₂ intermediate. Similar chemistry would be expected for glyceraldehyde. In this case, however, there are two possible intermediates i.e. α-oxo-η₂ and β-oxo-η₂ glyceraldehyde that can be formed depending on which of the OH groups interacts with the surface. Due to the presence of two OH groups in the molecule, disappearance of the ν(OH) stretching peak cannot be used to demonstrate the formation of these species. The change in the intensity of the ν(CO) stretch at 1076 cm⁻¹ corresponding to the secondary C-OH group, however, strongly suggests that reaction occurs at this site to preferentially form the α-oxo-η₂ (see Figure 4.5).
Upon further heating to 285 K, the HREEL spectrum indicates that C-C bond scission begins to take place, marked by the emergence of three-fold-hollow CO at 1889 cm\(^{-1}\), and the decrease in the intensity of the \(\delta\)(CCO) deformation at 630 cm\(^{-1}\). Unreacted surface species persist at this temperature, however, as indicated by the peaks between 950 to 1500 cm\(^{-1}\) and the \(\nu\)(OH) stretch at 3323 cm\(^{-1}\). By 300 K nearly all the glyceraldehyde has decomposed and by 350 K the spectrum is dominated by the \(\nu\)(CO) stretch for three-fold-hollow CO and the corresponding \(\nu\)(Pd-C) stretch at 278 cm\(^{-1}\). There is also a hint of some hydrocarbon fragments remaining on the surface as indicated by the weak \(\nu\)(CH\(_x\)) modes near 2900 cm\(^{-1}\). In contrast to glycolaldehyde, decomposition of glyceraldehyde does not result in the production of adsorbed acetylide intermediates. This may be a consequence of the lack of CH\(_2\) functionality at the \(\alpha\) carbon.

The HREEL spectrum of saturation exposure of glucose/Pd(111) at 115 K (Figure 4.4c) is similar to that of glyceraldehyde at this temperature. Tentative peak assignments based on comparisons to the glyceraldehyde/Pd(111) spectrum and that of solid- and vapor-phase glucose are given in Table 4.3. One important feature in the spectrum is the peak at 1715 cm\(^{-1}\) which is indicative of an aldehyde group bonded in an \(\eta_1\)(C=O) configuration. Note that the ring isomers of glucose which are more stable in the solid and gas phases\(^{113, 114, 116-119}\) do not contain an aldehyde group and there is no \(\nu\)(C=O) stretch in their IR spectrum\(^{113, 114}\) (Table 4.3). Thus, the presence of an intense \(\nu\)(C=O) stretch at 1715 cm\(^{-1}\) in the spectrum of the glucose/Pd(111) provides definitive evidence for ring opening upon adsorption.
Heating to 185 K causes little change in the spectrum, consistent with both glycolaldehyde and glyceraldehyde. It should be noted again, as with glycolaldehyde, that the \( \nu(\text{OH}) \) stretch is shifted lower from the vapor phase IR, pointing to possible interaction of the alcohol OH groups with the metal surface as well as possible intermolecular hydrogen bonding. At 230 K the intensities of the peaks between 600 and 950 cm\(^{-1}\), which are likely due to bending and deformation modes of the molecular backbone, decrease. More significant changes occur upon heating to 290 K, including disappearance of peaks indicative of backbone deformation and stretching modes between 600 and 950 cm\(^{-1}\), the formation of a \( \nu(\text{Pd-C}) \) stretch at 302 cm\(^{-1}\), almost complete disappearance of the \( \nu(\text{OH}) \) stretch, and most notably, the appearance of a peak at 1889 cm\(^{-1}\) corresponding to the formation of three-fold-hollow CO. Decomposition of the adsorbed glucose is complete by 350 K and the spectrum obtained at this temperature indicates that the surface is covered with three-fold-hollow CO and some small hydrocarbon fragments.

4.4 Discussion

This study demonstrates the use of UHV surface science techniques to investigate the reaction of complex aldoses on model catalytic surfaces and provides a detailed picture of the adsorption and reaction of glycolaldehyde and glyceraldehyde on Pd(111), as well as insights into the related reaction pathways for glucose. The TPD and HREELS results show similar reaction pathways for glycolaldehyde, glyceraldehyde and glucose on Pd(111). Adsorption at temperatures below 185 K occurs via interaction of the aldehyde functionality with the surface in an \( \eta_1(\text{C=O}) \) bonding configuration which converts to a
di-$\sigma$ $\eta_2$(C-O) configuration upon gentle heating. This is consistent with DFT calculations which also show the $\eta_1$(C=O) and di-$\sigma$ $\eta_2$(C-O) bonding configurations are the most stable, with the latter being slightly preferred by $\sim$0.35 eV. An important consequence of the strong interaction of the aldehyde group with Pd(111) is that it provides a driving force for ring opening in glucose upon adsorption, in contrast to its tendency to remain heterocyclic in the gas and condensed phases.

Further reaction of the di-$\sigma$ $\eta_2$(C-O) intermediates proceeds via O-H bond scission in the $\alpha$ position in all three molecules to form $\alpha$-oxo-$\eta_2$ species at temperatures near 200 K (see Figure 4.5). For glycolaldehyde this conversion was signified by the disappearance of the $\nu$(OH) and $\delta$(CCO) modes and for glyceraldehyde by disappearance of the $\nu$(C-OH) mode of the secondary alcohol group. At higher temperatures C-C and C-H bond cleavage occurs resulting in the formation of CO and adsorbed hydrogen. For glycolaldehyde some ethylidyne species are also formed which convert to acetylide at higher temperatures, and are a consequence of C-O bond scission. These species were not observed for glyceraldehyde and glucose which is likely due to the absence of a CH$_2$ group in the $\alpha$ position of the $\alpha$-oxo-$\eta_2$ intermediates.

A consequence of the importance of $\alpha$-oxo-$\eta_2$ intermediates in the reaction pathways for aldoses on Pd(111) is that simple alcohols or polyols (e.g., ethylene glycol), which lack the aldehyde functionality, are not adequate model compounds for biomass-derived sugars in mechanistic studies of heterogeneously catalyzed biomass reforming on metal surfaces.
4.5 Conclusions

UHV surface science techniques have been used to characterize the adsorption and reaction of aldoses, including glucose, on Pd(111). TPD and HREELS data in conjunction with DFT calculations have allowed the role of the aldehyde and alcohol functional groups in the initial adsorption of these molecules to be assessed and molecular bonding configurations to be determined. The surface reaction pathways and the evolution of the stable surface intermediates that form upon heating have also been elucidated. The following specific conclusions can be drawn from this study:

1. For all three aldoses, the carbonyl oxygen provides the principal bonding site to Pd(111) in the \( \eta_1(C=O) \) configuration at 115 K with transition into the more stable di-\( \sigma \) \( \eta_2(C-O) \) configuration upon gentle heating.

2. The stability of the \( \eta_1(C=O) \) adsorption configuration provides a driving force for ring opening in glucose upon adsorption on Pd(111).

3. Adsorbed \( \eta_2(C-O) \) glycolaldehyde and glyceraldehyde undergo O-H bond scission upon heating to 200 K to form \( \alpha \)-oxo-\( \eta_2 \) surface intermediates with a similar species being inferred for glucose.

4. C_2 and C_3 aldoses are more appropriate model compounds than simple alcohols and polyols in studies of the surface chemistry of glucose on metal catalysts as they have both alcohol and aldehyde functionalities which are important in the glucose reaction chemistry.
4.6 Supplemental Information: Determining Saturation Aldose Dosages

Initial TPD studies focused on identifying the dosage required to produce a saturation coverage of each reactant on Pd(111) and to further verify the production of glyceraldehyde and glucose vapors from the effusion cells. TPD spectra as a function of exposure for glycolaldehyde, glyceraldehyde, and glucose are presented in Figure 4.6. The glycolaldehyde spectra in Figure 4.6a show the emergence of the parent mass m/e 60 at 170 K for exposures greater than ~0.5 L. In addition to m/e 60, identical peaks for the other primary cracking fragments of glycolaldehyde, i.e. m/e 32, 31, and 29, were also observed (not shown in the figure) with relative intensities consistent with those in the mass spectrum of glycolaldehyde in the NIST mass spectrometry database. The m/e 60 peak can, therefore, be assigned to desorption of molecular glycolaldehyde. Since the onset of desorption of the molecular species occurred for a 0.5 L dose, this dose was used in the TPD and HREELS experiments described below which focused on characterizing the surface reactions of chemisorbed glycolaldehyde.

![Figure 4.6: Coverage variation TPD for (a) glycolaldehyde, (b) glyceraldehyde and (c) glucose.](image)

The analogous data for glyceraldehyde is shown in Figure 4.6b. In this case m/e 61, which is a primary cracking fragment, was used to monitor for glyceraldehyde
desorption. The molecular desorption spectra for glyceraldehyde were slightly more complex than those for glycolaldehyde with two separate desorption peaks at 214 and 281 K emerging for exposures greater than 0.25 L, with the higher temperature peak increasing in size more rapidly with coverage. While additional study is needed to determine the origin of each peak, it is possible that the peaks are due to the presence of both monomers and dimers in the adsorbed multilayers, with the dimers dissociating and desorbing at the higher temperature. Based on these data, a 0.25 L dose was chosen for use in subsequent TPD and HREELS experiments which focused on the reaction of glyceraldehyde on Pd(111).

As expected, the TPD results for glucose on Pd(111) in Figure 4.6c show that it is less volatile than the other aldoses with the molecular desorption peak appearing at 325 K. The figure shows data for m/e 73, with identical peaks also observed for the other primary cracking fragments for glucose reported in the NIST mass spectrometry database (e.g., m/e 61, 60, 43, and 31). Based on these data, a 0.4 L dose was chosen for use in subsequent TPD and HREELS experiments which focused on the reaction of chemisorbed glucose on Pd(111).
Chapter 5. Aldoses on Ni/Pd(111) Surfaces: A TPD Study*

Summary

The catalytic production of fuels and chemicals from biomass requires a greater understanding of the chemistry of biomass-derived sugars on advanced catalyst surfaces. This study examines the reaction of cellulosic derivative D-glucose and functional surrogates glycolaldehyde and glyceraldehyde on the bimetallic Ni/Pd(111) surface using temperature programmed desorption (TPD) in ultra high vacuum (UHV). It was found that the primary reaction pathway on the Ni/Pd system for all three molecules was dehydrogenation to produce CO and H₂. Additionally, it was found that of the surfaces studied, the reforming activity followed the trend Pd(111) > Pd-Ni-Pd ~ Ni-Pd-Pd > thick Ni/Pd. The Ni terminated surfaces were also found to produce ethylene at high temperatures and saw generally higher temperature and broader H₂ desorption peaks, suggesting a higher energy barrier for C-H bond scission.

5.1 Introduction

Growing concerns over the declining reserves of fossil fuels and the environmental impact of their use has motivated research in renewable energy resources and chemical feedstocks. As described in Chapter 1, cellulosic biomass is particularly attractive in this regard since it can be produced in a sustainable manner. Utilization of biomass as a feedstock for fuels and chemicals, however, is contingent on being able to convert its constituent molecules, such as xylose and glucose, into more useful products. The highly oxygenated nature of these polyols presents multiple challenges for this conversion, and catalysts optimized for selective C-H, C-C, O-H, and C-O bond scission are required in order to reach this goal.

The selective bond breaking chemistry required for reforming biomass-derived oxygenates into useful products is often performed using group 10 transition metal catalysts. This has motivated recent surface science studies of the reactivity of oxygenates on group 10 metal single crystal surfaces with the goal of elucidating the relevant reaction pathways and the factors that control selectivity for C-H and C-C bond breaking. In the majority of these studies, small molecules, such as ethanol or ethylene glycol, have been used as surrogates for the more complex sugars that are present in biomass. While such studies are useful and provide insight into the surface reactivity of specific functional groups, it is not clear whether they allow one to explore all the chemistry that is relevant to understanding reforming mechanisms for the more complex biomolecules.
In an effort to bridge the gap between mechanistic surface science studies of small oxygenate reactions on metal surfaces and the reaction of more complex aldoses found in biomass on these surfaces, we have previously used temperature programmed desorption (TPD) and high resolution electron energy loss (HREEL) spectroscopy to characterize the adsorption and reaction of aldoses (i.e. molecules that contain a single CHO group and have the general formula $C_n(H_2O)_m$), including glucose, on both Pd(111) and Pt(111) surfaces described in Chapter 3 and 4. In the study of the reaction of glycolaldehyde, glyceraldehyde, and glucose on Pd(111) presented in Chapter 4, it was shown that these molecules adsorb in an $\eta_1$(C=O) configuration where bonding occurs via the lone pair electrons on the carbonyl oxygen, with subsequent transition to an $\eta_2$(C-O) di-$\sigma$ bonding configuration. This is followed by $\alpha$-O-H bond scission resulting in an $\alpha$-oxo-$\eta_2$ intermediate which ultimately decomposes to CO and H$_2$. These results demonstrated the importance of using aldoses as functional surrogates for biomass-derived sugars instead of simple alcohols in fundamental surface science studies of biomass reforming on metal catalysts because the aldehyde moiety plays such an important role in the initial bonding of the molecule to the surface. Further study of the catalytic chemistry of these molecules is needed, however, in order to design catalysts with high selectivity for specific transformations such as deoxygenation or dehydrogenation.

Using bimetallic catalysts is one approach that has shown promise as a means to tailor the catalytic activity for specific reaction pathways. For example, as Chapter 1 highlights, recent experimental and theoretical studies of Ni/Pt bimetallics have
demonstrated that the local structure of the alloy can significantly affect reactivity. In particular it was shown that a metastable Ni-Pt-Pt(111) surface produced by depositing a monolayer of Ni on Pt(111) had a significantly higher activity for the dehydrogenation of simple alcohols and polyols to CO and H₂ compared to a Pt-Ni-Pt(111) sample where the Ni was in the subsurface layer (the Ni goes subsurface upon annealing above 600 K). DFT calculations have shown that the difference in the reactivity of these model catalysts correlates with the d-band center, showing increasing activity as it approaches the Fermi-level. Similar effects have also been predicted for the analogous Ni/Pd(111) system.

The goal of the present study was twofold: first to further demonstrate that surface science studies of complex biomolecules, such as glucose, on well defined surfaces are tractable and provide valuable insight into stable intermediates and reaction pathways, and second to determine if the Ni/Pd(111) bimetallic surfaces exhibit reactivity trends similar to those reported for the Ni/Pt(111) system. The specific reactants and surfaces that were investigated herein include glycolaldehyde, glyceraldehyde and glucose on Pd(111), Ni-Pd-Pd(111), Pd-Ni-Pd(111) and thick Ni/Pd(111).

5.2 Methods

The experiments in this investigation were performed in an ultra high vacuum (UHV) explained in detail within Chapter 2. A quartz crystal film thickness monitor (Maxtek Inc.) was used for monitoring the flux from the Ni deposition source, and dosing of glyceraldehyde and glucose molecules was performed using an auxiliary high vacuum chamber connected to the main chamber via a gate valve shown in Figure 2.5 and
described in Chapter 2. The Pd(111) single crystal from Princeton Scientific was 10 \, mm \times 5 \, mm \times 1 \, mm in size and was mounted on two tantalum posts allowing for resistive heating in excess of 1200 K and conductive cooling to 100 K from a liquid N\textsubscript{2} reservoir. Temperature was monitored using a chromel-alumel thermocouple spot-welded to the back of the crystal.

The Pd(111) single crystal was cleaned using repeated cycles of 2 kV Ar\textsuperscript{+} ion bombardment at room temperature, followed by annealing in vacuum for 15 mins at 1100 K and annealing in 2 \times 10^{-8} \text{torr} O\textsubscript{2} at 1100 K for 20 mins. Temperature programmed desorption (TPD) experiments were performed with a 3 K/s heating rate. Ni was deposited onto the Pd(111) surface using an evaporative Ni source comprised of 0.1 \, mm diameter high purity Ni wire that was tightly wrapped around a resistively heated 0.2 \, mm diameter tungsten filament. The Ni flux produced from the source was monitored using the quartz crystal film thickness monitor with Ni coverages on Pd(111) reported in monolayers (ML), with 1 ML being defined as $1.53 \times 10^{15} \text{atoms/cm}^2$, the density of Pd atoms on the Pd(111) surface. Preparation of the Ni/Pd(111) bimetallic surfaces was performed using the same technique as that for Ni/Pt(111) bimetallic surfaces used by Skopylyak et al.\textsuperscript{40-42, 124} and Yu et al.\textsuperscript{46} Ni-Pd-Pd surfaces were prepared by depositing 1 ML of Ni onto the clean Pd(111) surface at 300 K, whereas Pd-Ni-Pd surfaces were prepared by depositing 1 ML of Ni onto the clean Pd(111) surface at 600 K.

Glycolaldehyde was introduced into the vacuum system from a heated glass bulb containing crystalline glycolaldehyde dimer (Pfaltz and Bauer, 98%) attached to a variable leak valve that connected to the main UHV chamber as displayed in Figure 2.3.
The glycolaldehyde and dosing line were heated to 330 K to produce an appreciable vapor pressure for dosing into the UHV environment. More detailed explanations of the dosing setup are given in a previous publication by Yu et al.\textsuperscript{46} and in the previous chapters of this thesis. Glyceraldehyde and glucose had to be introduced into the system via the auxiliary vacuum chamber due to their low vapor pressures and thermal sensitivities. Molecular beams were produced using quartz effusion cells that could be resistively heated in a controlled manner to 370 and 400 K for glyceraldehyde and glucose, respectively. These molecular beams impinged on the crystal surface when the auxiliary chamber gate valve was opened. Verification of the production of glyceraldehyde and glucose vapors was obtained using mass spectrometry. A more in depth discussion of the application of this dosing methodology can be found in Chapters 2 and 4.

\section*{5.3 Results and Discussion}

In order to examine the reaction of glucose and the related model aldoses on Pd(111) and Ni/Pd bimetallics, TPD was performed for Pd(111), Ni-Pd-Pd, Pd-Ni-Pd and thick Ni/Pd surfaces dosed with glycolaldehyde, glyceraldehyde and glucose. A constant aldose exposure, corresponding to that required to obtain saturation, monolayer coverage on Pd(111), was used in each TPD experiment. The corresponding exposures for glycolaldehyde, glyceraldehyde and glucose were 0.5 L, 0.25 L and 0.4 L, respectively. It should be noted that for glyceraldehyde and glucose these Langmuir values are based on pressures measured using an ion gauge that was not in line of sight of the molecular beams and therefore cannot be used to calculate the total number of molecules impinging
on the sample. Data for this calibration of the saturation dose of each molecule can be found in the supplemental section of Chapter 4.

To verify that vapor-deposited Ni forms an epitaxial layer on Pd(111) and that this layer is catalytically unique compared to bulk Ni(111) in a manner analogous to that reported for Ni/Pt(111) by Skoplyak et al.,40 TPD studies of glycolaldehyde-dosed surfaces as a function of the Ni coverage were performed. In this series of experiments each sample was prepared starting with a clean Pd(111) surface followed by controlled deposition of the desired amount of Ni. As will be shown below, the primary reaction pathway for glycolaldehyde on all surfaces studied was dehydrogenation to produce \( \text{H}_2 \) and CO.

![Figure 5.1](image_url)

**Figure 5.1:** (a) CO desorption spectra for a 0.5 L exposure of glycolaldehyde on increasing coverages of Ni on Pd(111) and the (b) respective quantifications for CO yield.

Figure 5.1(a) shows the CO desorption spectra for the Pd(111) sample with increasing coverages of Ni exposed to 0.5 L glycolaldehyde. On Ni-free Pd(111), CO desorbs in a
single peak centered at 445 K. This peak temperature is indicative of CO adsorbed in three-fold hollow sites\textsuperscript{61, 101, 102, 126} and therefore indicates that C-H and C-C bond scission in the adsorbed glycolaldehyde occurs below this temperature. As the Ni coverage is increased from 0 to 0.75 ML, the CO desorption peak shifts from 445 K to 427 K. It is interesting that a single peak is still observed and not separate peaks for the bare and Ni-covered portions of the surface. This suggests that the Ni is forming an ordered overlayer that is modifying the electronic properties of the entire surface in such a way that it destabilizes the surface-CO interaction. Additionally, the area of the CO peak decreases by more than two-thirds as the Ni coverage is increased up to 0.75 ML as shown in Figure 5.1(b). While a small fraction of this change can be attributed to the production of ethylene on the Ni-covered surfaces (see below), the rest must be due to a decrease in the initial coverage of glycolaldehyde. This suggests that either the sticking coefficient for glycolaldehyde decreases with Ni coverage in the sub-monolayer Ni regime, or that the Ni blocks adsorption sites. The fact that glycolaldehyde readily adsorbs on Ni, as will be shown below, argues against Ni site-blocking and, therefore, supports the former explanation. As noted in the introduction, previous studies of the adsorption of small aldoses, including glycolaldehyde, on Pd(111), show that at temperatures below 200 K adsorption occurs through the aldehyde functionality resulting in the formation of both $\eta_1$ and $\eta_2$ intermediates.\textsuperscript{121} Assuming the surface-adsorbate bonding on Ni-Pd-Pd is similar, the decrease in the glycolaldehyde sticking coefficient with increasing Ni coverage up to 0.75 ML, indicates that the Ni adatoms alter the
surface electronic properties which affects the energetics of the aldehyde-surface interaction.

The data in Figure 5.1 also show that a dramatic change in the character of the surface occurs for Ni exposures between 0.75 ML and 1.5 ML. In this Ni coverage regime the total amount of CO desorbed for a 0.5 L glycolaldehyde dose rose to a value roughly half of that for the Ni-free Pd(111) surface. The amount of CO produced on the 1.5 ML Ni-Pd-Pd surface was also nearly the same as that obtained from the 3 ML thick Ni film. When the amounts of secondary products (ethylene and formaldehyde) are taken into account the data indicates that the initial glycolaldehyde coverage on the 1.5 ML and 3 ML Ni samples is close to that for the Ni-free Pd(111) surface. In addition to the change in CO peak area, a new lower temperature CO peak emerges at 365 K. Between 1 and 3 ML of Ni the high-temperature CO peak (427 K) decreases in intensity with a concomitant increase in the intensity of the low-temperature peak and, for the 3 ML Ni sample, the CO desorption spectrum is dominated by the low-temperature peak. Rapid change in the character of the surface for Ni coverages between 0 and 0.75 ML and then again from 0.75 ML to 1.5 ML demonstrates the unique reactivity of the Ni-Pd-Pd surface compared to bulk Ni.

Complete sets of TPD spectra for the reaction of glycolaldehyde, glyceraldehyde, and D-glucose on Pd(111), monolayer Ni-Pd-Pd, subsurface monolayer Pd-Ni-Pd, and thick Ni/Pd(111) samples are reported in Figure 5.2, Figure 5.3, and Figure 5.4. Quantification of the product yields are reported in Table 5.1. Hydrogen was omitted from this analysis due to the propensity of Pd to form bulk hydrides and the possibility that some
of the hydrogen may have diffused into the crystal, thereby rendering its quantification somewhat ambiguous.

Figure 5.2: TPD Spectra for a 0.5 L exposure of glycolaldehyde on Pd and Ni/Pd surfaces showing (a) CO, (b) H₂, (c) ethylene and (d) formaldehyde reaction products.

For glycolaldehyde (Figure 5.2), the reaction products CO, H₂, and CH₂O were observed for all four surfaces. Additionally, the Ni-terminated surfaces (Ni-Pd-Pd and thick Ni/Pd) were found to produce a trace amount of ethylene. The production of ethylene provides a distinguishing characteristic for surfaces with exposed Ni. The lack
of this product for the Pd-Ni-Pd surface, therefore, provides additional support for the conclusion that monolayer Ni goes subsurface following annealing at 600 K.

The CO desorption spectra in Figure 5.2(a) show that the CO peak for the Pd-Ni-Pd surface occurs at 424 K, which is intermediate between that for Pd(111) and Ni-Pd-Pd indicating that the subsurface Ni destabilizes the CO-surface bonding in a manner that is similar to that of Ni adatoms as observed in Figure 5.1. It should be noted that the CO peak at 338 K from the Ni-terminated surfaces is at a temperature lower than that expected for CO desorption from Ni(111), suggesting that it is a reaction limited product. In our previous HREELS study of aldoses on Pd(111) it was shown that decomposition of adsorbed glycolaldehyde is complete by 300 K. Thus, the reaction limited CO peak from the Ni-terminated surfaces at 383 K implies a higher stability for glycolaldehyde or glycolaldehyde-derived intermediates on these surfaces.

Table 5.1: TPD Reaction yields, reported in equivalent monolayers of CO, for 0.5 L glycolaldehyde, 0.25 L glyceraldehyde and 0.4 L glucose exposures on Pd and Ni/Pd surfaces. H$_2$ is omitted as a quantifiable product in all cases due to the tendency of H$_2$ to incorporate into the Pd bulk and produce ambiguous results.

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Product</th>
<th>Pd(111)</th>
<th>Pd-Ni-Pd</th>
<th>Ni-Pd-Pd</th>
<th>Thick Ni/Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Glycolaldehyde</strong></td>
<td>CO</td>
<td>0.30</td>
<td>0.18</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Ethylene</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.13</td>
</tr>
<tr>
<td><strong>Glyceraldehyde</strong></td>
<td>CO</td>
<td>0.46</td>
<td>0.36</td>
<td>0.33</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>Ethylene</td>
<td>-</td>
<td>-</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Glycolaldehyde</td>
<td>0.01</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>0.04</td>
<td>0.08</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>Glucose</strong></td>
<td>CO</td>
<td>0.38</td>
<td>0.31</td>
<td>0.31</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Ethylene</td>
<td>-</td>
<td>-</td>
<td>0.06</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>CO$_2$</td>
<td>0.02</td>
<td>0.03</td>
<td>0.05</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Only minor amounts of formaldehyde (Figure 5.2(d)) were produced on all surfaces except thick Ni/Pd, where the formaldehyde yield was slightly less than that of CO. For Pd(111) and Pd-Ni-Pd, the formaldehyde desorption temperature is close to that reported for desorption of molecular formaldehyde from both Ni(111)\textsuperscript{133} and Pd(111),\textsuperscript{90} indicating that they are desorption limited; however, for the Ni-terminated surfaces, H\textsubscript{2}CO was produced 25 K higher suggesting a reaction limited product. This again supports the conclusion that the Ni-terminated surfaces are less reactive toward glycolaldehyde compared to Pd(111) and Pd-Ni-Pd. Furthermore, note that the yield of H\textsubscript{2}CO from thick Ni/Pd approaches that of CO. This is an important feature, as it distinguishes the thick Ni/Pd surface from the Ni-Pd-Pd surface alloy, whose TPD features are otherwise similar. The production of formaldehyde for the thick Ni/Pd surface may be a result of an increased energy barrier for C-H scission resulting in the retention of the formaldehyde species after C-C scission of the glycolaldehyde surface intermediate.

The TPD results for the glyceraldehyde-dosed surfaces are shown in Figure 5.3. The major products for all surfaces again were CO and H\textsubscript{2}, with minor products ethylene, glycolaldehyde and methanol as summarized in Table 5.1. The trends in the CO desorption spectra in Figure 5.3(a) are similar to those for glycolaldehyde, with desorption-limited peaks for Pd-terminated surfaces, and the emergence a reaction-limited peak at 330 K for the Ni-terminated surfaces. The CO desorption curves for the Pd(111) and Pd-Ni-Pd surfaces are broader than those obtained for glycolaldehyde due to a low-temperature shoulder. The peak shape, however, is reminiscent of that obtained for high coverages of CO on Pd(111).\textsuperscript{101} With regards to H\textsubscript{2} desorption, Figure 5.3(b) shows
Figure 5.3: TPD spectra for a 0.25 L exposure of glyceraldehyde on Pd and Ni/Pd surfaces showing (a) CO, (b) H2, (c) ethylene and (d) glycolaldehyde reaction products.

a desorption-limited peak at 288 K\textsuperscript{100} dominating the spectrum from the Pd(111) and Pd-Ni-Pd surfaces. Also, similar to the glycolaldehyde results, the production of ethylene is observed only for the Ni-terminated surfaces above 600 K (Figure 5.3(c)), again distinguishing the Ni-Pd-Pd surface from Pd-Ni-Pd. Finally, it is notable that a small amount of glycolaldehyde and methanol (only glycolaldehyde is shown in the figure) were concomitantly produced at 288 K for the Ni-containing catalysts, with the largest amount being produced from the Pd-Ni-Pd surface. This suggests a lower barrier for
scission of the C-C bond between the α and β carbons in glyceraldehyde relative to the C-C bond between the carbonyl and α carbon for the Ni-Pd bimetallics.

Figure 5.4 presents the TPD results from the four surfaces dosed with glucose. Consistent with the simpler aldoses, glucose produced primarily CO and H₂ and the minor product ethylene, summarized in Table 5.1. Both the CO and ethylene desorption curves are nearly identical to those obtained for the glyceraldehyde-dosed surface, and reflect the congruence of chemistry between the functionally related aldoses. Again, this implies that the reactive intermediates have a higher energy barrier for bond scission indicated by the reaction-limited CO desorption on the Ni-terminated catalysts and that ethylene production only occurs on the Ni-terminated catalysts, as discussed above. However, in a divergence from the glyceraldehyde data, CO₂ was observed in the glucose TPD results, although only in trace quantities, as shown in Figure 5.4(d). H₂ was found to desorb from the Pd-terminated catalysts at 330 K, approximately 40 K higher than that for glyceraldehyde, though the Ni-terminated surfaces exhibited the broader, higher temperature H₂ desorption consistent with glyceraldehyde results.
Figure 5.4: TPD spectra for a 0.4 L exposure of glucose on Pd and Ni/Pd surfaces showing (a) CO, (b) H₂, (c) ethylene and (d) CO₂ reaction products.

For all molecules (glycolaldehyde, glyceraldehyde and glucose) and surfaces (Pd(111), Pd-Ni-Pd, Ni-Pd-Pd and thick Ni/Pd) studied, the major products were CO and H₂, consistent with a dehydrogenation pathway. The Pd-Ni-Pd and Ni-Pd-Pd catalysts showed similar CO yield and raised the question of how the two catalysts are different, if at all. When examining the TPD products, however, it is clear that the two catalysts are in fact different, as the Ni-Pd-Pd catalyst consistently produced ethylene at temperatures above 600 K, whereas the Pd-Ni-Pd catalyst did not produce any ethylene for the three
aldoses dosed. The production of ethylene is most likely a consequence of Ni termination on the catalyst surface, as the thick Ni/Pd catalyst exhibited a similar ethylene TPD peak. An additional distinguishing difference between the Pd-Ni-Pd and Ni-Pd-Pd catalyst is the more selective C-C scission for glyceraldehyde for the Pd-Ni-Pd catalyst, evidenced by the greater quantities of glycolaldehyde and methanol production, a consequence of C-C scission between the α and β carbons.

Figure 5.5: TPD Reforming yields for glycolaldehyde, glyceraldehyde and glucose on Pd(111) and Ni/Pd surfaces, reported in equivalent monolayers of CO. It is of note that different exposures of each aldose were used for each subset, but identical exposures of each aldose were used within each subset.

To draw dehydrogenation reforming activity comparisons between the four catalysts, one would ideally like to look at the H₂ yield of each catalyst for the given aldose reactant dose; however, as explained above, the tendency of H₂ to enter the Pd crystal bulk complicates quantification. Instead, CO was used as the benchmark for reforming yield, as total reforming chemistry would produce one CO molecule for every H₂
produced. Figure 5.5 shows the CO yields for each surface when dosed with equivalent coverages (calibrated as the saturation dose for each respective molecule on the Pd(111) surface) of one of the three aldoses. The most notable feature of these results are that for all three molecules, Pd(111) is clearly the more active reforming catalyst. Additionally, the reforming activity of the Pd-Ni-Pd and Ni-Pd-Pd bimetallic catalysts is indistinguishable for all three molecules. With regard to the thick Ni/Pd catalyst, it performs similarly to the Ni/Pd bimetals in the case of the smaller glycolaldehyde molecule, but as the size of the reactant is stepped up to C₃ glyceraldehyde and C₆ glucose, the reforming activity drops off noticeably. This may be linked to the much broader hydrogen TPD peaks for the Ni-terminated systems and the higher energy barriers for C-H scission, where C-H scission would be reaction limited and occurring in multiple stages at higher temperatures than the Pd terminated catalysts. In terms of general aldose reforming, the activity trend observed was Pd(111) > Pd-Ni-Pd ~ Ni-Pd-Pd > thick Ni. This is in contrast to the expected result that Ni-Pd-Pd would be the most active when taking cues from oxygenate reforming on the Ni/Pt bimetallic systems in previous publications.²⁰⁻²²,¹²⁴ While additional study is needed to determine the origins of this difference between the two systems, it is possible that the propensity for hydrogen to absorb into Pd and not Pt may play a role. Indeed, recent studies have shown that diffusion of hydrogen into Pd particles dramatically alters their activity for hydrogenation of alkenes,¹³⁴,¹³⁵ suggesting that hydrogen in the bulk may alter the electronic properties of the Pd surface.
5.4 Conclusion

The reactions of glycolaldehyde, glyceraldehyde and glucose have been characterized on Ni/Pd bimetallic catalysts using TPD. It was found that for Pd(111), Pd-Ni-Pd, Ni-Pd-Pd and thick Ni/Pd catalysts, the primary products were CO and H₂, indicative of a dehydrogenation reforming pathway. Activity for reforming was found to proceed in the order of Pd(111) > Pd-Ni-Pd ~ Ni-Pd-Pd > thick Ni/Pd for the reaction of simple aldoses. For all three aldoses studied, it was found that ethylene is produced only on the Ni terminated catalysts. This suggests higher energy barrier for C-H scission on the Ni-terminated catalysts, corroborated by broader and higher temperature H₂ desorption peaks.
Chapter 6. Selective Deoxygenation of Aldehydes: The Reaction of Acetaldehyde and Glycolaldehyde on Zn/Pt(111) Bimetallic Surfaces*

Summary

Temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) were used to characterize the adsorption and reaction of acetaldehyde and glycolaldehyde on Zn-modified Pt(111) surfaces. The barriers for both C-H and C-C bond cleavage in adsorbed aldehydes were found to be higher on Pt(111) decorated with Zn adatoms or containing a PtZn near-surface alloy, compared to Zn-free Pt(111). This results in stabilization of aldehydes adsorbed in an $\eta_2(C,O)$ bonding configuration and hinders formation of acyl intermediates as typically occurs on group 10 metals. Adsorbed $\eta_2(C,O)$ acetaldehyde and glycolaldehyde on Zn-modified Pt(111) were found to undergo selective C-O bond scission to produce adsorbed hydrocarbon intermediates and hydroxyl groups, while decarbonylation of acyl species to produce CO and hydrocarbon fragments was the primary pathway on the Zn-free surface. These results provide mechanistic insights that are useful for the design of hydrodeoxygenation catalysts for the upgrading of oxygenates derived from biomass, such as glucose and furfural.

* This chapter was published as McManus, J. R.; Martono, E.; Vohs, J. M., ACS Catalysis 2013, 3, 1739-1750.
6.1 Introduction

Supported metals play a pivotal role in catalyzing a range of complex hydrocarbon transformations required for the efficient production of fuels and chemicals from petroleum feedstocks. The proposed use of biomass as an alternate, renewable carbon source will also require metal catalysts to facilitate the upgrading of bio-oxygenates, such as glucose and xylose, to useful products.\textsuperscript{136-138} While many of the catalytic pathways required for biomass upgrading are similar to those used in petroleum refining, some are unique such as hydrogenolysis of the C-O bonds in aldoses and furfurals, which requires C-O bond scission and selective hydrogenation of C=O and C-OH groups in the presence of aromatic and C=C functionalities. As explained in Chapter 1, these reactions are particularly important for liquid fuels production from biomass where deoxygenation is necessary.

In most cases, monometallic catalysts are not particularly selective for these bio-oxygenate specific reactions. The use of bimetals has been proposed as one method to increase and tailor catalyst selectivity,\textsuperscript{120, 139, 140} and recently, mechanistic studies have started to appear in the literature in which the effect of alloying a highly catalytic metal with a second, less-reactive metal on the selectivity for these reactions has been explored. Examples include Ni-modification of Pt\textsuperscript{40-43} and Pd\textsuperscript{141} for bio-oxygenate reforming, Co- and Cu- modification of Pt\textsuperscript{58} and Ni\textsuperscript{57} for hydrodeoxygenation (HDO) of \textit{m}-cresol and furfural, alloying Ru,\textsuperscript{142, 143} Ag\textsuperscript{144} and Pd\textsuperscript{145} with Cu for glycerol hydrogenolysis, and Zn modification of Pt\textsuperscript{65} and Pd\textsuperscript{20, 61-64, 146, 147} for steam reforming of bioalcohols. The differences in reactivity of the bimetals compared to the monometallics is generally
attributed to alterations in the electronic band structure of the metal, and in many cases reactivity trends have been shown to correlate with the energy of the center of the alloy d-band.\textsuperscript{40, 42, 148-151}

![Figure 6.1: Schematics of surface intermediates: (a) η\textsubscript{1}(O) aldehyde, (b) di-σ η\textsubscript{2}(C,O) aldehyde, (c) acyl (termed acetyl when R = CH\textsubscript{3}), (d) alkoxide, (e) α-oxo-η\textsubscript{1} aldehyde, and (f) α-oxo-η\textsubscript{2} aldehyde.](image)

While long-range electronic effects in bimetals are clearly important, it is also possible that the second metal provides specific bonding sites for some intermediates. One such example of this is Sn-modification of Rh for selective hydrogenation of the aldehyde group in propionaldehyde and crotonaldehyde. For this system, Nishiyama et al.\textsuperscript{59} have reported that the carbonyl oxygen bonds via donation from the lone pair electrons into locally electron deficient exposed Sn sites. This results in an upright η\textsubscript{1}(O) bonding configuration (Figure 6.1a) for the carbonyl which suppresses interaction of the C=C group with the surface, effectively increasing the selectivity for hydrogenation of the aldehyde group versus the unsaturated C=C bond. Similarly, addition of more oxyphilic atoms like Zn to Pt,\textsuperscript{65} Fe to Pt\textsuperscript{152} and Fe to Ni\textsuperscript{54} have been proposed to provide specific binding sites for both aldehydes and alkoxides. On the basis of density functional
theory (DFT) results for aldehyde adsorption on Fe-modified Ni, Sitthisa et al.\textsuperscript{54} have proposed that the Fe atoms provide sites that preferentially bond the carbonyl oxygen in furfural (C\textsubscript{4}H\textsubscript{3}OCHO), leading to the formation of an $\eta_2$(C,O) adsorption complex (Figure 6.1b) with a weakened C-O bond that facilitates hydrogenolysis to produce 2-methylfuran (C\textsubscript{4}H\textsubscript{3}OCH\textsubscript{3}). In contrast, on Ni-only catalysts, less desirable decarbonylation to produce furan predominates. This observation has implications for biomass reforming since HDO of furfurals, which are produced by the dehydration of sugars, is a key step in many of the reaction pathways proposed for the upgrading of cellulosic biomass to value added fuels and chemicals.\textsuperscript{49,153}

PtZn bimetallics exhibit some properties similar to those mentioned above for SnRh, and FeNi. In particular, they are highly selective for the hydrogenation of the carbonyl group in $\alpha,\beta$-unsaturated aldehydes.\textsuperscript{60} Our group has recently demonstrated that adding Zn to Pt increases the barriers for C-H and C-C scission in adsorbed oxygenates,\textsuperscript{65} thereby stabilizing these species to higher temperatures which could help facilitate C-O hydrogenolysis. We have also shown that oxyphilic surface Zn atoms provide bonding sites for adsorbed alkoxides. Whether Zn-modified Pt surfaces are active for hydrogenolysis of carbonyl groups in a manner similar to that observed for FeNi has yet to be explored.

In the work reported herein we have used Zn-modified Pt(111) model catalysts to study the reaction pathways for oxygenates with aldehyde functionalities, namely, acetaldehyde and glycolaldehyde. The latter was chosen as a probe molecule based on previous studies which have shown it to be a good model surrogate for glucose in
mechanistic studies of surface reactions. Temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) data have allowed the stable surface intermediates and pathways to be determined for reaction on both PtZn near-surface alloys on Pt(111) and Pt(111) surfaces decorated with Zn adatoms. Specific sites that are active for C-O bond cleavage in adsorbed aldehydes have been identified and our results provide experimental verification of the HDO mechanism proposed by Sitthisa et al.

6.2 Experimental

Experiments in this investigation were performed using an ultrahigh vacuum (UHV) chamber described in detail within Chapter 2. The Pt(111) single crystal substrate (Goodfellow) was 10 mm in diameter and oriented to within ± 0.5°. It was cleaned by repeated cycles of 2 kV Ar⁺ ion bombardment for 30 min, annealing at 1100 K for 15 min in vacuum, and annealing in 2 × 10⁻⁸ torr O₂ at 1000 K for 20 min. The sample was spot-welded to two tantalum posts connected to the UHV sample manipulator, shown schematically in Figure 2.2, and could be resistively heated and cooled to 100 K by conduction from a liquid N₂ reservoir. HREEL spectra were collected in the specular direction with a 4 eV electron beam directed at 60° with respect to the surface normal, with an elastic peak count rate of between 20,000 and 200,000 cps and a full width half-maximum of 40 cm⁻¹. A heating rate of 4 K s⁻¹ was used in all TPD experiments.

Acetaldehyde (Acros Organics, 99.5%) and glycolaldehyde (Pfaltz and Bauer, dimer, 98%) were both introduced from a glass bulb attached to a heated, high-vacuum dosing line connected to the UHV chamber via variable leak valve, as described in Chapter 2.
The glycolaldehyde source, a crystalline dimer at room temperature, required gentle heating to 330 K to dissociate the dimers and produce sufficient vapor pressure for dosing into the main apparatus. The purity of both the acetaldehyde and the glycolaldehyde reagents was verified using the mass spectrometer on the UHV chamber. Dosages used for both molecules used in this study were chosen such that they produced a low-temperature desorption of the weakly adsorbed species, as to ensure surface saturation of the chemisorbed species.

Zn was deposited onto the Pt(111) surface using an evaporative Zn source consisting of a resistively heated tungsten filament wrapped with a coil of Zn wire (Alfa Aesar, 99.99%). The Zn flux was monitored using the quartz crystal microbalance (QCM), and we report the Zn coverages in effective monolayers, where one monolayer is assumed to be the density of Pt atoms on the Pt(111) surface, $1.51 \times 10^{15}$ atoms/cm$^2$. All Zn depositions were performed with the Pt(111) sample at or below room temperature. Two types of Zn-modified Pt(111) surfaces were used in this study: (1) surfaces decorated with Zn adatoms prepared by dosing Zn at or below room temperature, which we designate as Zn/Pt(111), and (2) surfaces in which the Zn was incorporated into the near surface region which we designate as PtZn/Pt(111). The latter were prepared by annealing a Zn/Pt(111) surface at 600 K for 2 min. The structure of near-surface PtZn alloys on Pt(111) produced in this manner have previously been characterized in detail by Ho et al. using X-ray photoelectron spectroscopy (XPS), X-ray photoelectron diffraction, and low-energy ion scattering. These studies show that for a PtZn/Pt(111)
sample prepared by depositing 1 ML of Zn followed by annealing at 600 K, the surface layer contains only ~5 at. % Zn, with the balance occupying the second and third layers.

6.3 Results

6.3.1 Reaction of acetaldehyde on Zn-modified Pt(111) surfaces

Acetaldehyde TPD experiments were initially performed in order to probe the reactivity of CHO groups on the Pt(111) and Zn-modified Pt(111) surfaces. Figure 6.2 shows TPD spectra from acetaldehyde-dosed Pt(111), 0.5 ML PtZn/Pt(111) alloy, and Zn/Pt(111) adatom surfaces with 0.2, 0.4, and 0.8 ML Zn coverages. In each experiment, 0.5 L acetaldehyde was dosed onto the sample at 100 K. For Zn-free Pt(111) (the bottom spectrum in each panel in Figure 6.2), molecular acetaldehyde desorbed in two peaks centered at 150 and 200 K. Though we monitored for several C₂ products like ethylene, acetylene, ethanol, and ketene, the only gaseous reaction products detected were CO and H₂, which appeared as desorption-limited peaks at 406 and 332 K, respectively. Additional, less-intense H₂ peaks are apparent between 400 and 600 K, which are attributable to the decomposition of surface methyl groups produced during acetaldehyde decomposition at lower temperatures. These results for Pt(111) are consistent with those reported previously in the literature.¹⁵⁶

The 0.5 ML PtZn/Pt(111) alloy surface was found to be substantially less reactive than Pt(111) with the majority of the acetaldehyde desorbing intact in two sharp peaks centered at 135 and 164 K (Figure 6.2a). Small amounts of CO and H₂ (Figure 6.2b,c) were also produced at temperatures similar to that observed for Pt(111). This is consistent
with previous studies of the reaction of alcohols on PtZn/Pt(111) alloys where these surfaces were found to be somewhat less reactive than Zn-free Pt(111).65

Figure 6.2: (a) CH$_3$CHO, (b) CO, (c) H$_2$, and (d) Zn TPD spectra obtained from Zn-modified Pt(111) surfaces following a 0.5 L CH$_3$CHO dose. The specific surfaces are indicated in the figure. Note the different temperature scale for panel (d).

Much more interesting chemistry was observed for the reaction of acetaldehyde on the adatom Zn/Pt(111) surfaces. On these surfaces, desorption of molecular acetaldehyde
occurred at 143 K with the size of this peak increasing with Zn coverage. Some small acetaldehyde peaks were also apparent at higher temperatures, the most noticeable being at 282 K for 0.4 ML Zn/Pt(111). The only gaseous reaction products evolved during TPD were again CO and H₂ demonstrating that, like Pt(111), these surfaces are active for both C-H and C-C bond scission. Note, however, that these products tended to be produced at higher temperatures than on Pt(111) suggesting that the Zn adatoms help stabilize the adsorbed intermediates.

For 0.2 ML Zn/Pt(111), CO desorbed in two peaks centered at 406 and 490 K with the latter having roughly twice the area of the former. The peak at 406 K is at the same temperature as that for desorption-limited CO from Zn-free Pt(111). This peak disappeared when the Zn coverage was increased to 0.4 ML or greater, indicating that it corresponds to CO adsorbed on Zn-free portions of the surface. The prominent, higher-temperature CO peak at 490 K decreased in intensity when the Zn coverage was increased to 0.4 ML, and was absent altogether for the 0.8 ML Zn/Pt(111) surface. The fact that the intensity of this peak goes through a maximum with increasing Zn coverage suggests that it is associated with species adsorbed on Pt sites that are modified by adjacent or nearby Zn adatoms. Note that since CO was the only carbon-containing gaseous product detected, acetaldehyde decomposition must also result in significant carbon deposition on the surface.

Complex behavior was also observed for the H₂ product during acetaldehyde TPD on the Zn-modified surfaces (Figure 6.2c). As noted above, the 0.5 ML PtZn/Pt(111) surface had relatively low reactivity toward acetaldehyde, and consequently only small amounts
H₂ were produced in a series of overlapping peaks between 300 and 550 K. For the much more active 0.2 ML Zn/Pt(111) adatom surface, H₂ was produced in two large peaks centered at 406 and 500 K with the former being twice the size of the latter. Consistent with the CO desorption spectra, the H₂ peaks became smaller with increasing Zn adatom coverage and also shifted to higher temperatures. Only a single, small H₂ peak at 470 K was present for the 0.8 ML Zn/Pt(111) sample.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Zn peak area</th>
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<td>0.8 ML Zn/Pt(111)</td>
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</tr>
<tr>
<td>0.4 ML Zn/Pt(111)</td>
<td>0.04</td>
</tr>
<tr>
<td>0.2 ML Zn/Pt(111)</td>
<td>0.02</td>
</tr>
<tr>
<td>0.5 ML PtZn/Pt(111)</td>
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</tr>
<tr>
<td>Pt(111)</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Zn desorption spectra were also collected during the acetaldehyde TPD experiments and are shown in Figure 6.2d. For both the alloy and the adatom surfaces the majority of the Zn desorbs in several overlapping peaks between 700 and 1100 K which is consistent with that reported previously for Zn-modified Pt(111). Note that the Zn adatoms react with the Pt(111) surfaces to form an alloy between 600 and 700 K during the TPD run, and thus the Zn desorption peaks in the 750-1100 K range are due to desorption of Zn from the alloy surface. For the adatom Zn/Pt(111) surfaces, an additional sharp Zn desorption feature is present between 640 and 680 K. The possible origins of this feature are addressed in the discussion below. These data also provide an additional measure of the Zn coverage for each sample. The relative Zn peak areas for each sample (arbitrarily

112
scaled) are listed in Table 6.1 and agree well with the amount of deposited Zn as determined by QCM.

Figure 6.3: HREEL spectra of 0.5 L acetaldehyde-dosed (a) Pt(111), (b) 0.5 ML PtZn/Pt(111), and (c) 0.5 ML Zn/Pt(111) as a function of temperature.

Table 6.2: Vibrational mode assignments for acetaldehyde and acetaldehyde adsorbed on various metal surfaces

<table>
<thead>
<tr>
<th>Frequency, cm⁻¹</th>
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<th>Infrared liquid</th>
<th>Raman</th>
<th>DFT</th>
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<th>Pt(111) 100 K</th>
<th>Pt(111) 200 K</th>
<th>Pt(111) 150 K</th>
<th>Pd(111)</th>
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<td>1115</td>
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<td>911</td>
<td>884</td>
<td>913</td>
<td>875</td>
<td>875</td>
<td>900</td>
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<td>763</td>
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<td>762</td>
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<td>750</td>
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<td>-</td>
<td>-</td>
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<tr>
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<td>-</td>
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<td>-</td>
<td>-</td>
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<td>600</td>
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<td>550</td>
<td>523</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Data from this work marked in bold. *Peak not assigned in reference.
To identify stable reaction intermediates and provide additional insight into the pathways for the reaction of acetaldehyde on the Zn-modified Pt(111) surfaces, HREEL spectra as a function of temperature were collected for surfaces dosed with 0.5 L acetaldehyde and are displayed in Figure 6.3. For the Zn-free Pt(111) surface at 100 K (Figure 6.3a), the spectrum is dominated by peaks at 2940, 1700, 1408, 1115, 750, and 523 cm\(^{-1}\), which is consistent with that reported previously by Zhao et al.\(^{156}\) for acetaldehyde on Pt(111) at 90 K. Mode assignments for each peak in the spectrum are presented in Table 6.2 and were made via comparison to the infrared and Raman spectra\(^{157}\) of acetaldehyde and the DFT simulations of acetaldehyde on Pt(111) by Delbecq and Vigné,\(^{158}\) which are also included in the table. The close correspondence between the HREEL spectra and the DFT simulation demonstrates that the acetaldehyde adsorbs in an \(\eta_1(O)\) configuration in which bonding occurs through the lone pair electrons on the carbonyl oxygen, shown schematically in Figure 6.1a.

Heating of the sample to 200 K resulted in the disappearance of the \(\nu(C=O)\) and \(\gamma(CH)\) stretches at 1700 and 750 cm\(^{-1}\), respectively, accompanied by the emergence of a stretch at 1580 cm\(^{-1}\) and a shift of the \(\delta(CCO)\) stretch at 523 cm\(^{-1}\) to 607 cm\(^{-1}\), all of which are indicative of C-H scission at the aldehyde carbon and the formation of an acetyl intermediate (Figure 6.1c). As shown in Table 6.2, this result is consistent with acetyl formation on Pd(111) reported by Davis et al.\(^{90}\) Further heating to 300 K and above resulted in decomposition of the acetyl intermediate into CO and H\(_2\), as indicated by the emergence of the peaks at 1816 and 2055 cm\(^{-1}\), which correspond to the \(\nu(C=O)\)
mode of bridge and atop bound CO, respectively, and the appearance of CO and H₂ in the TPD spectra (Figure 6.2b,c).

Table 6.3: Vibrational mode assignments for 0.5 L acetaldehyde-dosed Zn-modified Pt(111).

<table>
<thead>
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<th>mode</th>
<th>frequency, cm⁻¹</th>
</tr>
</thead>
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<tr>
<td></td>
<td>100 K</td>
</tr>
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<td>-</td>
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<td>νCH₃, νCH₂</td>
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<td>νacetylC=O</td>
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<tr>
<td>δCH</td>
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<tr>
<td>δCH, νCC</td>
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</tr>
<tr>
<td>νCO</td>
<td>-</td>
</tr>
<tr>
<td>ν(acetyl)C=O</td>
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</tr>
<tr>
<td>νCH₃, νCC</td>
<td>880</td>
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<tr>
<td>γCH</td>
<td>755</td>
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<tr>
<td>δacetylCCO</td>
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</tr>
<tr>
<td>δCCO, νPtO</td>
<td>516</td>
</tr>
<tr>
<td>νPtC</td>
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</tbody>
</table>

Data from this work marked in bold.

Table 6.4: Vibrational mode assignments for acetaldehyde-dosed Zn/Pt(111)

<table>
<thead>
<tr>
<th>mode</th>
<th>frequency, cm⁻¹</th>
</tr>
</thead>
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<td>Acetaldehyde-dosed</td>
</tr>
<tr>
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<td>Zn/Pt(111), 400 K</td>
</tr>
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<td>νCH</td>
<td>3034, 2922, 2840</td>
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<td>δCH₃</td>
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<td>1115</td>
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<td>νCC</td>
<td>1022</td>
</tr>
<tr>
<td>ρCH₃, γCH₂</td>
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<tr>
<td>τCH₂</td>
<td>880</td>
</tr>
<tr>
<td>ρCH₂, ρCH</td>
<td>647</td>
</tr>
</tbody>
</table>

Data from this work marked in bold. aWeak.
For the PtZn/Pt(111) surface alloy, the HREEL spectrum of the acetaldehyde-dosed surface at 100 K, Figure 6.3b, is nearly identical to that obtained from Pt(111); however, upon heating to 200 K a few notable differences stand out, particularly the emergence of a vibrational loss at 458 cm\(^{-1}\) as well as intense losses at 1094 and 1150 cm\(^{-1}\). These peaks most likely correspond to the formation of a di-\(\sigma\) \(\eta_2\) surface intermediate, as predicted by Delbecq and Vigné,\(^{158}\) and as shown schematically in Figure 6.1b. The frequencies for the di-\(\sigma\) \(\eta_2\) acetaldehyde intermediate are juxtaposed to the experimental vibrational mode assignments for 0.5 L acetaldehyde on 0.5 ML PtZn/Pt(111) in Table 6.3. In addition to the peaks for di-\(\sigma\) \(\eta_2\) acetaldehyde, the spectrum also contains small peaks at 600 and 1580 cm\(^{-1}\), which, as discussed above, suggest the formation of some acetyl species. Upon heating to 300 and 400 K, these surface intermediates decompose similarly to that on Pt(111), forming H\(_2\) and CO products. Unlike on Zn-free Pt(111), however, the CO produced from these reactions only occupies the atop sites, as indicated by a vibrational loss at 2002 cm\(^{-1}\) and the lack of losses for bridging species between 1800 and 1870 cm\(^{-1}\). This is consistent with previous studies that have shown that CO prefers the atop sites on PtZn alloy surfaces.\(^{65}\)

A 0.5 ML Zn/Pt(111) surface was chosen as a representative Zn adatom surface for the acetaldehyde HREELS studies. The spectra obtained from this surface are displayed in Figure 6.3c. As expected, the spectrum at 100 K is nearly identical to that observed for acetaldehyde on the other two surfaces and is characteristic of molecularly adsorbed acetaldehyde (see Table 6.3). Unlike the other two surfaces, however, the intact acetaldehyde molecule persists to 200 K with no evidence for C-H bond scission or the
formation of an acetyl intermediate. This indicates that the Zn adatoms help stabilize the adsorbed molecular acetaldehyde and apparently increase the barrier for C-H bond scission. This is consistent with that reported for methoxide and formaldehyde intermediates on a Zn-modified Pd(111) surface.\(^6\)

Heating to 300 K, however, did cause significant changes in the vibrational spectrum of the adsorbed species, particularly the emergence of a small loss at 647 cm\(^{-1}\) and a relatively intense loss at 1022 cm\(^{-1}\), the disappearance of the aldehyde \(\nu(C=O)\) stretch at 1705 cm\(^{-1}\), and most strikingly, the emergence of a \(\nu(OH)\) stretch at 3575 cm\(^{-1}\), which is characteristic of an adsorbed hydroxyl group. The simultaneous disappearance of the aldehyde \(\nu(C=O)\) stretch and appearance of the hydroxyl \(\nu(OH)\) peak provide direct evidence for cleavage of the C=O bond. Cleavage of only the C=O bond in acetaldehyde would likely result in the formation of a surface ethylidene (=CH-CH\(_3\)) intermediate. Ethylidene is unstable on most metal surfaces, but when isolable gives rise to a \(\nu(CC)\) peak near 975 cm\(^{-1}\),\(^{16}\) which is absent in the HREEL spectrum of the acetaldehyde-dosed surface allowing it to be ruled out. Other possible C\(_2\) intermediates include vinyl (-CH=CH\(_2\)), vinylidene (=CH=CH\(_2\)), ethylidyne (≡C-CH\(_3\)) and ethylene (C\(_2\)H\(_2\)). The vibrational spectrum of both vinyl\(^{162-165}\) and vinylidene\(^{166}\) species on metal surfaces contain characteristic \(\gamma(CH_2)\), \(\delta(CH)\), and \(\nu(C=C)\) peaks between 900 and 1000 cm\(^{-1}\), 1230 and 1280 cm\(^{-1}\), and 1500 and 1600 cm\(^{-1}\), respectively. The absence of these peaks in the spectra obtained from the acetaldehyde-dosed 0.5 ML Zn/Pt(111) surface heated to 300 and 400 K allow these intermediates to also be ruled out. As shown in Table 6.4, the peaks in the 400 K spectrum at 2922, 1358, and 1115 cm\(^{-1}\) match well with the \(\nu(CH)\),
δ(CH₃) and ν(CC) peaks expected for an ethylidyne intermediate, suggesting that this species may be formed. This, however, leaves the peaks at 1416, 1022, and 647 cm⁻¹ in the spectrum of the acetaldehyde-dosed sample unaccounted for. These peaks do align reasonably well with those reported previously for ethylene adsorbed in a di-σ configuration with the 1416 cm⁻¹ stretch corresponding to a δ(CH₂) scissor mode, the 1022 cm⁻¹ loss to the ν(CC) stretch, and the losses at 647 and 880 cm⁻¹ to the ρ(CH₂) and τ(CH₂) modes, respectively (see Table 6.4). Acetylide and acetylene intermediates were also considered but provided poor matches with the vibrational spectra of the adsorbed intermediates. These observations lead us to propose that following C-O scission in adsorbed acetaldehyde, both di-σ bonded ethylene and ethylidyne species are formed. In addition to C=O bond cleavage, the production of ethylidyne from adsorbed acetaldehyde also requires cleavage of the carbonyl C-H bond, while formation of di-σ ethylene requires a 1,2 hydride shift. Presumably, the former also provides the hydrogen for the formation of the adsorbed hydroxyl group.

6.3.2 Reaction of glycolaldehyde on Zn-modified Pt(111) surfaces

TPD data obtained from clean and Zn-modified Pt(111) surfaces dosed with 1 L of glycolaldehyde are displayed in Figure 6.4. The primary reaction pathway on Pt(111) is complete dehydrogenation to produce CO and H₂ which appear as desorption-limited peaks at 397 and 320 K, respectively. Small amounts of CH₃OH and CH₂O and are also produced at 242 and 320 K, respectively. These products are represented by spectra for m/e 31 and 30 in Figure 6.4, and were identified based on analysis of multiple m/e values and their known cracking patterns. Also note that both m/e 30 and 31 are in the mass
spectrometer cracking pattern for glycolaldehyde and thus also exhibit a large peak at 183 K which corresponds to molecular glycolaldehyde desorption.

The data for the PtZn/Pt(111) near-surface alloy samples, which were synthesized using 0.1, 0.5, and 1.0 ML of Zn, were similar to that of Pt(111) with the overall dehydrogenation activity decreasing somewhat with increasing Zn concentration. The CO peak did broaden considerably on the alloy surfaces and shifted down to 368 K. This temperature is consistent with that reported for CO-dosed PnZn/Pt(111) indicating that it is desorption limited. The H\textsubscript{2} peak also broadened, and shifted up in temperature to 368 K. As was the case for Pt(111), small amounts of CH\textsubscript{2}O (356 K) and CH\textsubscript{3}OH (273 K) were also observed for the acetaldehyde-dosed PtZn/Pt(111) surfaces.

Consistent with TPD results for acetaldehyde, significantly different chemistry was observed for the reaction of glycolaldehyde on Zn/Pt(111) Zn-adatom surfaces compared to PtZn/Pt(111) and Pt(111). As shown in Figure 6.4, which includes data for 0.1 and 0.4 ML Zn/Pt(111) dosed with 1 L glycolaldehyde, the low-temperature peaks corresponding to molecular glycolaldehyde are dramatically reduced in intensity relative to PtZn/Pt(111) and Pt(111), while at the same time the primary reaction products, CO and H\textsubscript{2}, are produced at significantly higher temperatures compared with these other surfaces. For the 0.1 ML Zn/Pt(111) both CO and H\textsubscript{2} are produced in two peaks centered at 418 and 535 K. This result is analogous to that observed for acetaldehyde (and also that reported for surfaces dosed with formaldehyde and methanol\textsuperscript{65}), though the high-temperature peak for glycolaldehyde is approximately 40 K higher, indicating a slightly increased barrier for decomposition of glycolaldehyde to CO and H\textsubscript{2} compared to acetaldehyde. Again, similar
to the acetaldehyde results, the 0.4 ML Zn/Pt(111) sample only exhibited the higher-
temperature, reaction-limited CO and H₂ peaks at 531 K. This result further indicates that
the Zn adatoms help stabilize the surface intermediates to higher temperatures. Unlike the
PtZn alloy sample, the Zn/Pt(111) adatom samples do not produce appreciable amounts
of formaldehyde or methanol from glycolaldehyde as shown in Figure 6.4d and e, again
supporting the conclusion that the Zn adatoms stabilize the surface intermediates and
prevent low-temperature C-C scission.

Figure 6.4: TPD spectra obtained following a 1 L glycolaldehyde dose on various Zn-modified
surfaces. Desorption products include (a) HOCH₂CHO, (b) CO, (c) H₂, (d) CH₂O, (e) CH₃OH, and (e)
an undetermined product with m/e fragments 45 and 43.
For the glycolaldehyde-dosed Zn adatom surfaces, a relatively small quantity of a side product which gave rise to peaks at 215 K in the \textit{m/e} 45 and 43 spectra with a 1.25 intensity ratio was observed (see Figure 6.4f and Table 6.5). Peaks at other \textit{m/e} values were not observed above the baseline level of the spectra. The most likely species that would give rise to significant \textit{m/e} 45 and 43 signals are isopropyl alcohol and acetoin (C$_4$H$_8$O$_2$), although it seems unlikely that either of these would be produced via the surface reaction of glycolaldehyde. We, therefore, postulate that one of these molecules may be present as an impurity in the glycolaldehyde sample.

HREEL vibrational spectra as a function of temperature for clean Pt(111), 0.5 ML PtZn/Pt(111), and 0.4 ML Zn/Pt(111) dosed with 1 L glycolaldehyde are displayed in Figure 6.5a,b,c, respectively. The spectra for glycolaldehyde on Pt(111) are similar to those reported previously\textsuperscript{155} and show the presence of molecular glycolaldehyde at 115 K. Individual peak assignments are given in Table 6.6. For comparison, the reported vibrational peak positions and assignments for glycolaldehyde vapor\textsuperscript{106} and glycolaldehyde physisorbed on Pd(111)\textsuperscript{154} are also included in the table. Heating the glycolaldehyde-dosed Pt(111) surface to 200 K caused two notable changes in the
Figure 6.5: HREEL spectra of 1 L glycolaldehyde-dosed (a) Pt(111), (b) 0.5 ML PtZn/Pt(111), and (c) 0.4 ML Zn/Pt(111) as a function of temperature.

Table 6.6: Vibrational mode assignments for glycolaldehyde on various surfaces.

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<th>mode</th>
<th>frequency, cm(^{-1})</th>
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</tr>
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<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>(\gamma)CH, (\gamma)OH</td>
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<td>775</td>
<td>736</td>
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</tr>
<tr>
<td>(\delta)CCO, (\delta)OH</td>
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<td>639</td>
<td>620</td>
<td>-</td>
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<tr>
<td>vM-O, vM-C</td>
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<td>-</td>
<td>531</td>
<td>531</td>
<td>n.r.</td>
<td>515</td>
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</tbody>
</table>

Data from this work marked in bold.

HREEL spectrum, the disappearance of the v(OH) peak at 3377 cm\(^{-1}\) and a shift in the position of the v(C=O) peak from 1715 to 1610 cm\(^{-1}\). The former demonstrates the
dissociation of the O-H group, while the latter is indicative of the carbonyl group bonding to the surface in the $\eta_1$ configuration shown in Figure 6.1a. Heating to 300 K results in C-C bond scission, as evidenced by the decrease of the $\nu$(CC) peak at 917 cm$^{-1}$ and additional dehydrogenation as evidenced by the emergence of peaks at 2039 and 1791 cm$^{-1}$ which are indicative of the $\nu$(CO) mode of atop and bridging CO species. Further decomposition is apparent at higher temperatures and the spectrum at 400 K contains losses indicative of adsorbed CO and small hydrocarbon fragments. The spectrum of the glycolaldehyde-dosed PtZn/Pt(111) alloy surface at 115 K was similar to that obtained for Pt(111) and contains peaks consistent with physisorbed glycolaldehyde (see Table 6.6). Heating to 200 K results in the decrease in intensity of the $\nu$(OH) peak at 3386 cm$^{-1}$, the emergence of a weak $\nu$(C=O) stretch at $\sim$1640 cm$^{-1}$, characteristic of an $\eta_1$ aldehyde, as well as the disappearance of the loss at 620 cm$^{-1}$. These changes are also similar to those observed for Pt(111) and indicate that the glycolaldehyde molecule can undergo O-H scission to form an alkoxide intermediate, shown schematically in Figure 6.1d, or bond to the surface via the lone pair electrons of the carbonyl oxygen. If both interactions occur simultaneously, an $\alpha$-oxo-$\eta_1$(C=O) intermediate would be formed (Figure 6.1e). This would constrain the molecular backbone somewhat, which might account for the disappearance of the $\delta$(CCO) loss at 620 cm$^{-1}$. Also note that the continued presence of the $\gamma$(CH) stretch at 745 cm$^{-1}$ argues against acyl formation.

Further heating to 250 and 300 K sees the disappearance of the $\nu$(C=O) and $\nu$(OH) stretches and the emergence of the stretch at 2017 cm$^{-1}$ characteristic of atop CO. Additionally, between 250 and 300 K, the intensity of the $\nu$(CC) peak at 853 cm$^{-1}$
considerably decreases which is consistent with C-C bond scission and CO formation. This result is also consistent with the TPD data which show the production of small amounts of formaldehyde and methanol in this temperature range. Continued heating to 350 K and above results in the shift of the peak at 507 cm\(^{-1}\) to 446 cm\(^{-1}\), the decrease in intensity of all the glycolaldehyde-related peaks, the persistence of the atop-site CO loss at 2017 cm\(^{-1}\), and the beginnings of a small peak at 1758 cm\(^{-1}\) associated with some bridge-site CO, all consistent with the decomposition of the surface intermediates to CO and H\(_2\).

Figure 6.5c displays the HREEL spectrum for the 1L glycolaldehyde-dosed 0.4 ML Zn/Pt(111) adatom surface, which displays chemistry that differs from that of the clean Pt(111) and PtZn alloy surfaces. At 115 K, the vibrational losses are again characteristic of adsorbed glycolaldehyde with vibrational mode assignments listed in Table 6.6. Intact OH groups are shown by the peak at 3353 cm\(^{-1}\) and an intact aldehyde group is demonstrated by the \(\nu(C=O)\) at 1705 cm\(^{-1}\). As shown by the TPD data, heating to 200 K causes desorption of weakly adsorbed molecular glycolaldehyde, resulting in a vibrational spectrum indicative of the chemisorbed species. The main new features in this spectrum include a decrease of the \(\nu(OH)\) stretch at 3353 cm\(^{-1}\), the appearance of a peak at 1656 cm\(^{-1}\) indicative of the \(\nu(C=O)\) mode of an \(\eta_1\) aldehyde, and strong \(\delta(CH_2), \delta(CH)\), and \(\nu(CO)\) losses at 1412, 1341, and 1085 cm\(^{-1}\), respectively. By 250 K, a relatively stable surface intermediate is formed that persists up to 400 K. This intermediate is marked by a lack of peaks in the \(\nu(OH)\) and \(\nu(C=O)\) ranges and well-defined peaks at 2855, 1412, 1341, 1216, 1050, 871, and 375 cm\(^{-1}\), with respective assignments in Table
6.6. The disappearance of the \( \nu(OH) \) stretch indicates dissociation of the O-H group and the formation of a surface-O bond. The peak at 1050 cm\(^{-1} \) can be assigned to the \( \nu(CO) \) mode of this end of the molecule. This observation is consistent with that reported for methanol on the adatom surface which also dissociates in this temperature range to form methoxide species.\(^{65} \) Since it seems unlikely that C=O bond cleavage would occur at 250 K, we attribute the disappearance of the \( \nu(C=O) \) peak at 1656 cm\(^{-1} \) to bonding of the carbonyl group with the surface in a di-\( \sigma \), \( \eta_2 \) configuration. This would be expected to also give rise to a \( \nu(CO) \) peak near 1085 cm\(^{-1} \). The intensity of this peak, however, would be relatively small because of the C-O bond axis being oriented nearly parallel to the surface. Together with the alkoxide bonding, this di-\( \sigma \) \( \eta_2 \) aldehyde could assume an \( \alpha \)-oxo-\( \eta_2 \) aldehyde configuration, as shown in Figure 6.1f.

As noted above, the intermediate giving rise to these peaks is relatively stable between 250 and 400 K. A small \( \nu(C=O) \) peak at 1975 cm\(^{-1} \) indicative of atop CO does emerge with increasing temperature, but this peak may be at least partially due to adsorption of CO from the background. There are a few other subtle features in the spectra, especially at 400 K, that suggest the formation of some secondary species. These include the re-emergence of a small peak at 3532 cm\(^{-1} \) indicative of the \( \nu(OH) \) mode of a surface hydroxyl, a shoulder at 3000 cm\(^{-1} \) on the \( \nu(CH) \) peak, and a small peak at 1568 cm\(^{-1} \), which is attributable to either the \( \nu(C=O) \) mode of an acyl, or perhaps more likely the formation of a C=C double bond. The formation of the surface hydroxyl group suggests C-O scission in a manner analogous to that described above for acetaldehyde on the Zn/Pt(111) surface.
Further heating to 500 K caused additional changes in the v(CH\textsubscript{x}) peak structure in the 2800-3000 cm\textsuperscript{-1} range favoring the 3000 cm\textsuperscript{-1} peak, as well as a decrease in the intensity of the 1341 and 1050 cm\textsuperscript{-1} peaks and a shift in the 871 cm\textsuperscript{-1} peak to a lower frequency. This, in combination with the relative increase in atop-site CO with respect to the other energy loss peaks, suggests C-C scission and decomposition to CO and H\textsubscript{2}. By 600 K, nearly all of the features of the glycolaldehyde intermediates are gone, leaving behind CO and small hydrocarbon fragments.

6.3.3 HREELS of EtOH on 0.4 ML Zn/Pt(111)

As noted above, there is evidence for C-O bond scission in both acetaldehyde and glycolaldehyde adsorbed on the Zn/Pt(111) adatom surface. For glycolaldehyde, this bond cleavage could potentially occur in either the carbonyl or the alcohol functional groups. To help determine whether this reaction pathway is specific to the carbonyl group, HREEL spectra as a function of temperature were collected for a 0.4 ML Zn/Pt(111) surface dosed with ethanol. These spectra are displayed in Figure 6.6 and the peak positions and assignments are listed in Table 6.7. As emphasized in the table, between 200 and 400 K the spectra are consistent with an adsorbed ethoxide intermediate and contain the characteristic v(CO) mode of this species at 1017 cm\textsuperscript{-1}. Upon heating to higher temperatures the ethoxide decomposes to produce CO, H\textsubscript{2}, and adsorbed carbon. No C-O bond scission and formation of surface hydroxyls is observed, suggesting the deoxygenation pathway for acetaldehyde and glycolaldehyde is specific to the aldehyde carbonyl.
Figure 6.6: HREEL vibrational spectra for 1 L ethanol on the 0.4 ML Zn/Pt(111) surface.

Table 6.7: Vibrational mode assignments for ethanol and ethoxide species.

<table>
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<tr>
<th>frequency cm⁻¹</th>
<th>Ethanol¹¹</th>
<th>Ethanol</th>
<th>Ethoxide</th>
<th>Ethoxide¹⁰⁶</th>
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<td>0.4ML Zn/Pt(111) 115 K</td>
<td>0.4ML Zn/Pt(111) 400 K</td>
<td>Pd(111) 200 K</td>
</tr>
<tr>
<td>νOH</td>
<td>3230</td>
<td>3221</td>
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<td>-</td>
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</tr>
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</tr>
<tr>
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Data from this work marked in bold

6.4 Discussion

The results of this study provide insight into how Zn atoms incorporated into or adsorbed onto a Pt surface influence the energetics of bond scission and the reaction pathways for
adsorbed oxygenates. Consistent with previous studies,\textsuperscript{156} acetaldehyde adsorbed on Pt(111) was found to undergo C–H bond scission at the carbonyl carbon to form an acetyl intermediate near 200 K. This species undergoes additional dehydrogenation and C–C bond scission between 200 and 300 K to form CO, H\textsubscript{2}, and adsorbed hydrocarbon fragments. In contrast, for PtZn/Pt(111) alloy surfaces, acetaldehyde remains largely intact desorbing at 164 K, with C–H bond cleavage to form an acetyl intermediate being only a minor reaction pathway. The lack of significant acetaldehyde dissociation indicates that either the activation barrier for C–H bond cleavage is higher or the reaction products are less stable on the alloy surface compared to that on Pt(111). For glycolaldehyde the increased production of methanol and formaldehyde between 230 and 350 K, which retain all the C–H bonds in the reactant, also suggests a higher barrier for C–H bond cleavage on the alloy surface. These results are also consistent with that reported previously for the reaction of alcohols on both PtZn/Pt(111)\textsuperscript{66} and PdZn/Pd(111)\textsuperscript{61,62,64} alloy surfaces.

It is noteworthy that the significant decrease in C–H bond activation on PtZn/Pt(111) compared to Pt(111) occurs in spite of the fact that the outermost layer of the alloy contains only 5\% Zn with the remaining Zn being distributed in the second and third layers (see discussion above).\textsuperscript{66} This indicates that the change in reactivity of the surface upon Zn incorporation is not due to Zn simply blocking Pt sites, but rather to alteration of the electronic properties of the surface. The fact that large differences were observed for small Zn concentrations also suggests that the Zn induces a relatively long-range
electronic effect. This conclusion is similar to that reported previously for Zn-modified Pd(111) surfaces.\textsuperscript{61-64, 102}

While the alteration of the activity of Pt(111), with respect to acetaldehyde and glycolaldehyde, upon alloying with a small amount of Zn was significant, even more dramatic changes were observed for Pt(111) surfaces decorated with Zn adatoms. Before discussing the reaction pathways observed on these surfaces it is important to recognize that the observed chemistry cannot be attributed solely to adsorption and reaction directly on Zn adatom sites. As we have shown in a previous study of the reactivity of Zn-modified Pt(111) surfaces,\textsuperscript{65} monolayer Zn films on Pt(111) are unreactive toward both methanol and formaldehyde with these species adsorbing molecularly at temperatures below 200 K and desorbing intact upon heating. Carbon monoxide was also found not to adsorb on ML Zn films at temperatures above 200 K. The low reactivity of the 0.8 ML Zn/Pt(111) surface toward acetaldehyde observed in the present study is consistent with these previous observations.

In contrast to Pt(111) where acetaldehyde undergoes C-H bond scission at temperatures below 200 K to form an acetyl intermediate which then decomposes to CO, H\textsubscript{2} and adsorbed CH\textsubscript{x} between 200 and 350 K, the HREELS results indicate that on Zn/Pt(111) an \( \eta_2(C,O) \) intermediate is formed which remains intact to \( \sim 350 \) K. Note that this is consistent with the barrier for C-H bond scission being higher on Zn-modified Pt(111) compared to clean Pt(111) as discussed above for the alloy surface. This difference is also readily apparent in the TPD data where the desorption-limited H\textsubscript{2} peak at 332 K for acetaldehyde-dosed Pt(111) is replaced by reaction-limited H\textsubscript{2} peaks.
between 375 and 550 K for Zn/Pt(111). As shown in Figure 6.7, we postulate that the Zn adatoms play a direct role in formation and stabilization of the η2(C,O) aldehyde intermediate by providing the bonding site for the O with the carbonyl carbon interacting with an adjacent Pt. This scenario is consistent with the high affinity of Zn for oxygen and the observation of Zn oxidation (as determined by XPS) by Zn-bound methoxides on methanol-dosed Zn/Pt(111).

The HREELS data show the formation of adsorbed hydroxyls upon heating the η2(C,O) aldehyde intermediate to between 300 and 400 K providing definitive evidence for C-O bond scission. This is an important result since it could provide a pathway for selective deoxygenation of biomass-derived oxygenates which contain aldehyde functionalities, such as glucose or furfural. In the case of acetaldehyde, this deoxygenation pathway produces ethylene and ethylidyne intermediates (Figure 6.7) which during TPD ultimately decompose to carbon and hydrogen. Recognize, however, that under steady-state hydrodeoxygenation conditions these intermediates are likely to be hydrogenated to produce stable hydrocarbon products with the hydroxyls reacting to form water.

It is interesting that during acetaldehyde TPD on the Zn/Pt(111) surfaces where C-O scission occurred, a sharp Zn desorption peak was observed at 660 K. During TPD in the absence of other adsorbed species, the Zn adatoms on Zn/Pt(111) become incorporated into the surface upon heating to ~600 K and then desorb at higher temperatures. We speculate that the OH groups that are formed on Zn adatoms during acetaldehyde
decomposition prevent the Zn from becoming incorporated into the surface and thus facilitate their desorption at a lower temperature.

**Acetaldehyde**

**Ethanol**

**Glycolaldehyde**

Figure 6.7: Proposed pathways and intermediates for the adsorption and reaction of acetaldehyde, ethanol and glycolaldehyde on Zn/Pt(111) adatom surfaces.

The TPD and HREELS data for glycolaldehyde on Zn/Pt(111) indicate mechanistic similarities to that observed for acetaldehyde, including increased barriers for C-H bond activation, an $\eta_2$(C,O) aldehyde intermediate in which the O interacts with a Zn adatom,
and C-O bond scission between 300 and 400 K. It is important to recognize for glycolaldehyde that it is feasible for C-O scission to occur at either the alcohol or the aldehyde functionalities. Data for the reaction of methanol\textsuperscript{65} and ethanol on Zn/Pt(111) surfaces, however, argue for the latter. For all three molecules, methanol, ethanol, and glycolaldehyde, HREELS shows low-temperature O-H scission and a shift in the $\nu$(C-O) peak, which is indicative of the formation of an alkoxide; although, for methanol and ethanol (Figure 6.6) C-O scission at the alkoxide moiety is not observed, thus it would also not be expected for glycolaldehyde. Furthermore, in our previous study of the reaction of methanol on Zn/Pt(111), it was demonstrated that O-H scission was facilitated by the Zn adatoms.\textsuperscript{65} Combined these results indicate the formation of the $\alpha$-oxo-$\eta_2$ glycolaldehyde intermediate shown in Figure 6.7. Analogous to acetaldehyde, the carbonyl group in this species undergoes C-O scission upon heating to 350 K. For glycolaldehyde this results in the formation of a vinyl alkoxide intermediate. Evidence for this includes the $\nu$(C=O) stretch at 1568 cm\textsuperscript{-1} as well as the strengthening of a $\rho$(CH) rocking mode at 1216 cm\textsuperscript{-1}, features common for surface bound vinyl groups.\textsuperscript{163-165} Though vinyl groups are normally quite reactive on Pt surfaces, the geometric constraints imposed by the alkoxide surface linkage likely prevent the $\pi$ electrons of the vinyl from interacting with the surface.
As shown schematically in Figure 6.8a, on group 10 metals (Ni, Pd, Pt) aldehydes typically undergo C-H scission to form acyl intermediates followed by decarbonylation to form a hydrocarbon and CO.\textsuperscript{54, 90, 144} The TPD and HREELS data obtained in this study demonstrate this pathway for both acetaldehyde and glycolaldehyde on Pt(111). In the context of upgrading oxygenates produced from biomass, such as glucose and furfural, to useful fuels and chemicals, this pathway generally needs to be avoided since it results in the loss of a carbon atom. Selective deoxygenation pathways, especially those involving carbonyl groups, are much more desirable since they produce more stable molecules with higher octane numbers. As noted in the introduction, alloying a highly active group 10 metal with a second, less-reactive metal has been proposed as one approach to alter the decarbonylation/deoxygenation selectivity to favor the deoxygenation pathway.\textsuperscript{54, 152} The recent study by Sitthisa et al. of the reaction of furfural and H\textsubscript{2} over Ni and NiFe bimetallic catalysts provides an excellent demonstration of this.\textsuperscript{54} They observed that a
Ni/SiO₂ catalyst was highly selective for decarbonylation to produce furan (C₄H₄O) and CO. In contrast, over a NiFe/SiO₂ catalyst, decarbonylation was significantly suppressed and the primary product was 2-methylfuran, which is produced via hydrogenolysis of the carbonyl group. On the basis of DFT calculations, they proposed that the reduction in decarbonylation was due to stabilization of an η₂(C,O) furfural intermediate via interaction of the carbonyl oxygen with an oxyphilic Fe atom and that this bonding configuration results in a weakening of the C-O bond thereby facilitating its dissociation.

The Zn/Pt(111) system is similar to the NiFe catalysts studied by Sitthisa et al.⁵⁴ in that it consists of a group 10 metal, Pt, modified by a less reactive oxyphilic metal, Zn. Our results for the reaction of both acetaldehyde and glycolaldehyde on Zn/Pt(111) are also consistent with those in the Sitthisa et al.⁵⁴ study and, furthermore, provide direct experimental confirmation of their proposed mechanism. In particular, as shown in Figure 6.8b, the addition of the second oxyphilic metal, Zn, was found to both provide a bonding site for the carbonyl oxygen, and increase the barrier for C-H bond scission, which is required for the formation of the acyl intermediate in the decarbonylation pathway. Combined, these factors lead to the formation of stable η₂(C,O) intermediates which are susceptible to C-O bond cleavage.

6.5 Conclusions

The TPD and HREELS results for the reaction of acetaldehyde and glycolaldehyde on Zn-modified Pt(111) surfaces obtained in this study lead to the following general conclusions: (1) alloying Pt with Zn decreases the activity for C-H and C-C bond cleavage, thereby stabilizing adsorbed oxygenate intermediates to higher temperatures;
(2) the increased barriers for C-H bond scission on PtZn/Pt(111) and Zn/Pt(111) surfaces hinder the formation of acyl intermediates from adsorbed aldehydes, which effectively decreases the selectivity for decarbonylation; (3) interaction of the carbonyl oxygen with Zn atoms stabilizes aldehyde bonding in an $\eta_2$(C,O) configuration, facilitating selective C-O bond cleavage at higher temperatures via the weakening of the C=O bond relative to that in the parent aldehyde. In addition to elucidating how Zn alters the reactivity of Pt toward aldehydes, the mechanistic insights obtained in this study are useful for the design of catalysts that are active for the selective deoxygenation of the aldehyde functionalities in biomass-derived oxygenates, such as glucose and furfural.
Chapter 7. Reaction of Glyceraldehyde and Glucose on Zn-modified Pt(111) Surfaces

Summary

The high oxygen content and multiple functional groups in biomass-derived platform molecules like glucose provide a major challenge in biomass conversion to value-added fuels and chemicals. Understanding the role of multiple functionalities in the reaction on catalytically relevant surfaces, particularly with regard to deoxygenation chemistry, is paramount. In this study, temperature programmed desorption and high resolution electron energy loss spectroscopy were utilized to identify the role of the multiple functionalities of glucose and model aldose glyceraldehyde in their reactions on Pt(111) and Zn-modified Pt(111) surfaces. Comparisons were drawn to similar data for model molecules acetaldehyde and glycolaldehyde. For all four molecules, dehydrogenation to form an acyl intermediate, followed by decarbonylation to form CO and H₂ occurred on Pt(111). Also, with all molecules studied, addition of Zn to the Pt(111) surface caused an increase in the barrier for C-H and C-C bond scission resulting in stabilization of surface intermediates to much higher temperatures than on Pt(111). The Zn/Pt(111) surface was additionally found to be active for alcohol dissociation to form Zn-bound alkoxides, and in the case of polyols glyceraldehyde and glucose, these multiple alkoxide bonds

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geometrically prevented the $\eta_2$(C,O) aldehyde bonding configuration and subsequent carbonyl deoxygenation that was observed with smaller C$_2$ molecules acetaldehyde and glycolaldehyde. These results help elucidate the role of multiple alcohol functionalities in biomass-derived oxygenates in the reaction over catalytically relevant surfaces, and highlight the potential of using alloy effects (such as Zn-modification of Pt shown herein) to modify catalytic chemistry.
7.1 Introduction

As described in Chapter 1, the potential of cellulosic biomass as a renewable carbon feedstock has motivated considerable research on its conversion into useful chemicals and fuels. Almost all proposed approaches for the utilization of cellulose in this manner rely on its initial depolymerization to produce glucose monomers, which are then transformed into the desired products through various chemistries, including reforming, isomerization, pyrolysis, and hydrodeoxygenation, among others.

The high oxygen content and functionalization of glucose and other biomass-derived oxygenates presents a significant challenge for their utilization as platform molecules. For example, glucose has a 1:1 C:O ratio and deoxygenation is necessary to yield fuel components like alkanes and olefins or value added compounds like 5-hydroxymethylfurfural. Developing heterogeneous catalysts that are selective for these deoxygenation pathways is currently a very active research area. On highly catalytically active Group 10 metals, glucose tends to undergo decarbonylation followed by further decomposition producing mainly syngas and other low value products. The addition of a second metal is one approach that is being explored to obtain more targeted deoxygenation chemistries. The influence of the second metal on the electronic properties of the bimetallic catalyst is clearly important and numerous studies have shown that reactivity often correlates with the energy of the alloy d-band center. Another way bimetallics can be used to control deoxygenation selectivity is through the formation of specific sites that have unique reactivities. For example, density
functional theory (DFT) calculations by Sitthisa et al.\textsuperscript{54} indicate that on a Ni/SiO\textsubscript{2} catalyst, biomass-derived furfural preferentially decarbonylates to furan, which proceeds through an acyl intermediate; however, on bimetallic FeNi/SiO\textsubscript{2} catalysts, cleavage of the carbonyl C-O bond occurs shifting the selectivity towards the more desired 2-methylfuran deoxygenation product. Their calculations indicate that this reaction is facilitated by bonding through the carbonyl group in an $\eta_2$(C,O) configuration in which the O interacts with an oxyphilic surface Fe site and the carbon interacts with an adjacent Ni site. This proposed mechanism involving a bimetallic site has recently been corroborated experimentally in our study of the reaction of biomass model compounds acetaldehyde and glycolaldehyde on Zn-modified Pt(111) surfaces, presented in Chapter 6.\textsuperscript{178} In that study it was shown that the aldehyde functionality dehydrogenates to form an acyl on Pt(111), subsequently decarbonylating to form CO and H\textsubscript{2}; whereas on the Pt(111) surface decorated with Zn atoms, dehydrogenation activity is greatly decreased and $\eta_2$(C,O) bonded intermediates undergo C-O bond cleavage at relatively low temperatures.

Although our previous studies of simple model compounds acetaldehyde and glycolaldehyde provided valuable insights into the enhancement of deoxygenation activity upon the addition of an oxyphilic metal, such as Zn, to a Group 10 metal, these molecules still fall short in capturing the complexity of more biomass-relevant oxygenates such as glucose. Particularly, the previously studied molecules lack the multiple alcohol functionalities that are characteristic of the polyol glucose. This makes the C\textsubscript{3} aldose glyceraldehyde an appropriate model compound to study as it is the
smallest aldose to contain polyol functionality with both a primary and secondary alcohol. To explore how this increased functionality affects surface reactivity, herein we have expanded our previous studies of the Zn/Pt(111) system to include glyceraldehyde and glucose.

7.2 Methods

Experiments were performed in an ultrahigh vacuum (UHV) chamber described in detail in Chapter 2. Auxiliary to the main UHV chamber and separated by a gate valve was a high vacuum dosing chamber containing effusion cells which were used to dose glyceraldehyde and glucose into the main chamber. The Pt(111) single crystal substrate (Goodfellow) was cleaned using repeated cycles of 2 kV Ar\(^+\) ion bombardment, annealing under vacuum at 1100 K, and annealing at 1000 K under \(2 \times 10^{-8}\) torr O\(_2\). The single crystal was mounted to the sample manipulator via spotwelding onto two tantalum metal posts which could be resistively heated, or conductively cooled through contact with a liquid N\(_2\) reservoir. Temperature programmed desorption (TPD) experiments were conducted with a 4 K s\(^{-1}\) heating rate, and HREEL data was collected in the specular direction with a 4 eV electron beam directed at 60° with respect to the surface normal, producing a typical elastic peak intensity of 100,000 cps and full width half-maximum of 5 meV.

Zn/Pt(111) adatom surfaces were prepared by vapor depositing Zn from a coil of Zn wire (Alfa Aesar, 99.99%) wrapped around a resistively heated tungsten filament onto the room temperature Pt(111) crystal, and the extent of Zn deposition was monitored by an in-plane QCM. All Zn coverages are reported in effective monolayers, where one
monolayer is assumed to be the density of Pt atoms on the Pt(111) surface, $1.51 \times 10^{15}$ atoms cm$^{-2}$. The Zn-modified Pt(111) surface alloy has been previously characterized by Ho et al.$^{66}$ using X-ray photoelectron diffraction and low energy ion scattering. In that study it was shown that adsorbed Zn atoms remain on the surface for temperatures below 600 K, while at higher temperatures they diffuse subsurface.

Acetaldehyde (Acros Organics, 99.5%) and glycolaldehyde (Pfaltz and Bauer, dimer, 98%) were both dosed from a heated glass bulb connected via high-vacuum dosing line to a variable leak valve for controlled introduction into the main UHV apparatus, as described in Chapter 2. Glyceraldehyde (DL-glyceraldehyde dimer, 97%, Aldrich) and glucose (D-(+)-glucose, 99.5 %, Sigma) were introduced into the main UHV chamber via resistively heated quartz effusion cells contained in the high vacuum auxiliary dosing chamber as explained in detail in the previous chapters.$^{141, 154, 155}$ The separate dosing apparatus with quartz effusion cell allowed for line-of-site dosing of the low vapor pressure solid crystalline glucose and glyceraldehyde without decomposition that would otherwise occur in the heated dosing line used for acetaldehyde and glycolaldehyde. The glyceraldehyde and glucose had to be heated to 370 K and 400 K, respectively, to produce a molecular beam sufficient for dosing from the auxiliary chamber. Mass spectrometry showed that only glyceraldehyde or glucose and no decomposition or pyrolysis products were produced from the effusion cells.
7.3 Results

7.3.1 Acetaldehyde and Glycolaldehyde on Pt(111) and Zn/Pt(111)

As noted in the introduction, we have previously characterized the adsorption and reaction of acetaldehyde and glycolaldehyde on Pt(111) and Zn-modified Pt(111) surfaces in Chapter 6. A subset of this data will be presented to provide a useful comparison with data collected for glyceraldehyde and glucose. HREEL spectra for Pt(111) and Zn/Pt(111) dosed with 0.5 L acetaldehyde at 115 K and then heated to 200 and 400 K are displayed in Figure 7.1. On the Pt(111) surface, acetaldehyde is found to undergo C–H bond cleavage to form an acetyl intermediate by 200 K, as indicated by the \( \nu_{\text{acetyl}}(\text{C}=\text{O}) \) at 1580 cm\(^{-1}\) (Figure 7.1a). Upon heating to higher temperatures this intermediate primarily undergoes decarbonylation yielding CO, as indicated by the atop and bridge site CO \( \nu(\text{CO}) \) stretches at 2055 and 1816 cm\(^{-1}\), respectively, and small hydrocarbon fragments. This result was further corroborated by TPD where the observed products were desorption-limited CO and H\(_2\) at 406 and 332 K, respectively. This reaction pathway is also consistent with that reported by Zhao et al.\(^{156}\) for acetaldehyde on Pt(111).

Significantly different chemistry was observed for acetaldehyde on Zn/Pt(111) compared to Pt(111). Adsorbed acetaldehyde does not form an acetyl intermediate on this surface, but instead bonds in an \( \eta_2(\text{C},\text{O}) \) configuration. This species is relatively stable on Zn/Pt(111) remaining largely intact up to 400 K, at which point cleavage of the C-O bond occurs resulting in the formation of adsorbed surface hydroxyl and ethylidyne intermediates. This deoxygenation pathway is signified in the HREELS data in Figure
7.1b by the appearance of a hydroxyl ν(OH) stretch at 3575 cm\(^{-1}\) upon heating to 400 K. As discussed in Chapter 6, TPD and HREELS data indicate that the formation of the \(\eta_2(C,O)\) intermediate occurs through interaction of the carbonyl oxygen with an oxyphilic Zn atom.\(^{178}\) The weakening of the C=O bond in the \(\eta_2(C,O)\) species relative to that in adsorbed \(\eta_1\) acetaldehyde or acetyl facilitates cleavage of the C-O bond.

![Figure 7.1: HREEL spectra for 0.5 L acetaldehyde deposited on (a) Pt(111) and (b) 0.5 ML Zn/Pt(111) surfaces.](image)

Similar to acetaldehyde, glycolaldehyde was found to undergo relatively facile decarbonylation on Pt(111). The HREELS data in Figure 7.2a show the nearly complete decomposition of glycolaldehyde to CO by 400 K, as indicated by the atop and bridge ν(CO) stretches at 2039 and 1791 cm\(^{-1}\), respectively. Like acetaldehyde, glycolaldehyde was more stable on 0.4 ML Zn/Pt(111) than on Pt(111). As shown by the HREELS data
in Figure 7.2b, at 200 K this molecule bonds to the surface via the aldehyde functionality in an \( \eta_1(O) \) configuration (given by the \( \eta_1 v(C=O) \) loss at 1656 cm\(^{-1}\)). Upon heating to 250 K the \( v(O-H) \) of the hydroxyl group between 3200 and 3500 cm\(^{-1}\) disappears indicating that this end of the molecule undergoes O-H bond scission to form an alkoxide. Additional evidence for this include a sharpening and shift in the position of the \( v(C-O) \) stretch that now appears 1050 cm\(^{-1}\) along with the appearance of a strong \( v(Zn-O) \) stretch at 375 cm\(^{-1}\), which also indicates this reaction takes place at a Zn site. Upon heating to 400 K a \( v(OH) \) mode reappears in the HREEL spectrum at 3532 cm\(^{-1}\). This result is consistent with that observed for acetaldehyde, reacting along the deoxygenation pathway via cleavage of the carbonyl C-O bond. As discussed in detail in our previous paper,\(^{178}\) many of the features in the HREELS spectrum at 400 K can be assigned to a vinyl alkoxide species. Note, however, that the appearance of a relatively strong \( v(CO) \) peak at 2026 cm\(^{-1}\) indicates that decarbonylation competes with the deoxygenation pathway that leads to the formation of the vinyl alkoxide. Indeed, the HREELS data suggest that the ratio of decarbonylation to deoxygenation is much higher for glycolaldehyde compared to acetaldehyde.
Figure 7.2: HREEL spectra for 1 L glycolaldehyde dosed on (a) Pt(111) and (b) 0.4 ML Zn/Pt(111) surfaces.

7.3.2 Glyceraldehyde on Pt(111) and Zn/Pt(111)

Figure 7.3 displays TPD results obtained from Pt(111), 0.1 ML Zn/Pt(111) and 0.4 ML Zn/Pt(111) surfaces dosed with 0.5 L glyceraldehyde at 115 K. The primary desorption products on all three surfaces were C₃H₆O₃, CO, CO₂, and H₂. On Pt(111) (the bottom curve in each panel in Figure 7.3), molecular glyceraldehyde desorbed in two peaks centered at 230 K and 300 K. The glyceraldehyde that remained on the surface underwent relatively facile decomposition producing exclusively CO and H₂, with the former desorbing in a primary peak at 386 K and a shoulder at ~440 K, and the latter desorbing in two sharp peaks at 333 and 386 K. Both the H₂ and CO peak temperatures are within the range expected for desorption-limited products, but the appearance of multiple H₂
peaks suggests that at least a portion of these products are reaction limited. These TPD results are consistent with the decarbonylation/decomposition pathway observed for acetaldehyde and glycolaldehyde on Pt(111). HREELS results presented below provide additional evidence for these pathways.

Addition of Zn to the Pt(111) surface resulted in a number of interesting changes in the surface chemistry. For both 0.1 and 0.4 ML Zn/Pt(111) adatom surfaces, the amount of molecular glyceraldehyde which desorbed intact at low temperature (230 K) was substantially less than that from clean Pt(111). Additionally, and more strikingly, the CO and H₂ products were produced at higher temperatures than on Pt(111) with reaction-limited CO and H₂ peaks occurring at 551 K for the 0.4 ML Zn/Pt(111) and 530 K for the 0.1 ML Zn/Pt(111). In addition to this high-temperature CO and H₂ desorption, the 0.1 ML Zn/Pt(111) adatom surface displayed a lower-temperature CO peak at 416 K, consistent with desorption from unaltered Pt(111) sites. The higher-temperature decomposition products on the Zn-modified surfaces are consistent with that reported for methanol,⁶⁵ acetaldehyde and glycolaldehyde,¹⁷⁸ and can be attributed to reaction on bimetallic Zn-Pt sites. It is noteworthy that the CO product from glyceraldehyde on Zn-modified Pt(111) is produced at temperatures above that reported for acetaldehyde and glycolaldehyde, suggesting a higher stability for the glyceraldehyde-derived surface intermediate. Also, in concert with the high-temperature CO and H₂ peaks on the adatom surfaces, there was a small quantity of CO₂ produced at 551 K which indicates that some C-O scission has occurred.
Figure 7.3: TPD of 0.5 L glyceraldehyde on Pt(111), 0.1 ML Zn/Pt(111), and 0.4 ML Zn/Pt(111) surfaces. Desorption products include (a) molecular glyceraldehyde, (b) CO, (c) H\textsubscript{2}, and (d) CO\textsubscript{2}. Scaling factors relative to the H\textsubscript{2} spectra are indicated in each pane.

To gain a better understanding of the pathways and intermediates involved in the adsorption and reaction of glyceraldehyde, HREEL spectra as a function of temperature were collected for the Pt(111) and 0.4 ML Zn/Pt(111) surfaces dosed with glyceraldehyde. Figure 7.4 displays a HREEL temperature sequence for a 0.5 L glyceraldehyde-dosed Pt(111) surface. The spectrum at 200 K is consistent with that expected for molecularly adsorbed glyceraldehyde with specific peak assignments given in Table 7.1. For comparison, the IR spectrum of glyceraldehyde vapor\textsuperscript{112} and the
HREEL spectrum of glyceraldehyde adsorbed on Pd(111)\textsuperscript{154} are also included in the table. Heating to 250 K and then 300 K resulted in several changes in the spectrum of the adsorbed species, the most notable being a shift in the ν(C=O) peak from 1705 cm\textsuperscript{-1} to that of an acyl carbonyl at 1598 cm\textsuperscript{-1}, the appearance of a new δ(CCO) mode at 550 cm\textsuperscript{-1}, and a significant decrease in the intensity of the γ(C-H) peak at ~725 cm\textsuperscript{-1}. Together these changes indicate the formation of an acyl intermediate via scission of the C-H bond on the carbonyl carbon. This is consistent with the chemistry observed for the smaller aldehydes on Pt(111) as discussed above.\textsuperscript{156, 178} Also note that upon heating to 300 K the intensity of the ν(OH) peak at 3344 cm\textsuperscript{-1} decreased considerably, suggesting dissociation of at least some of the hydroxyl groups. Further heating to 350 K resulted in C-C and C-H scission in the adsorbed intermediates leading to the decomposition product CO, giving rise to the two intense ν(CO) losses at 1800 and 2039 cm\textsuperscript{-1} for bridge and atop bound CO, respectively, and their corresponding ν(Pt-C) stretches at 385 and 455 cm\textsuperscript{-1}. Also observed at this temperature are some hydrocarbon fragments which have δ(CH\textsubscript{x}) and ν(CH\textsubscript{x}) peaks between 1300-1450 cm\textsuperscript{-1} and 2800-3100 cm\textsuperscript{-1}, respectively. The decomposition of the adsorbed hydrocarbon fragments releases hydrogen leading to the broad, overlapping H\textsubscript{2} desorption peaks between 450 and 650 K in Figure 7.3c.
Figure 7.4: HREELS temperature sequence for 0.5 L glyceraldehyde dosed onto a clean Pt(111) surface.

HREEL spectra for a 0.5 L glyceraldehyde-dosed 0.4 ML Zn/Pt(111) surface are displayed in Figure 7.5. At 200 K, 30 K below the desorption temperature for molecular glyceraldehyde, the spectrum corresponds to glyceraldehyde with vibrational losses (listed in Table 7.2) nearly identical to those obtained for glyceraldehyde on clean Pt(111) at 200 K. Briefly heating to 250 K to desorb any weakly bound glyceraldehyde caused a decrease in the intensity of the $\nu$(OH) stretch at 3325 cm$^{-1}$ and the $\tau$(OH) torsional mode at 632 cm$^{-1}$. This, along with the appearance of a small peak at 372 cm$^{-1}$, which can be assigned to a $\nu$(Zn-O) stretch,$^{65,178,179}$ suggests the onset of O-H scission.
Table 7.1: Vibrational mode assignments for glyceraldehyde on various surfaces

<table>
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<tr>
<th>mode</th>
<th>frequency, cm⁻¹</th>
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<th>Pt(111)b¹⁴</th>
<th>Pt(111)b¹⁵</th>
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<td>725</td>
<td>-</td>
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<td>678, 632</td>
<td>632</td>
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<td>-</td>
<td>550</td>
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<td>-</td>
<td>278</td>
<td>-</td>
<td>385</td>
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</table>

ᵃNot assigned in reference. ᵇThis work. n.r. not resolved.

Also at 250 K, the ν(C=O) stretch shifts from 1721 cm⁻¹ to 1617 cm⁻¹ which indicates an η₁(O) configuration for the carbonyl group where bonding to the surface is through one of the oxygen lone pairs. After heating to 300 K neither the ν(OH) or τ(OH) peaks are evident, suggesting that O-H scission is complete by this temperature. Additionally, there is a downward shift in the 2° and 1° alcohol ν(C-O) stretches which now appear at 1085 and 1020 cm⁻¹, respectively (see Table 7.2). This, along with the disappearance of the ν(OH) peak and the appearance of the intense ν(Zn-O) stretch at 372 cm⁻¹, all point to formation of alkoxide intermediates. The spectrum also still contains a ν(C=O) stretch at 1617 cm⁻¹ which is characteristic of an η₁(O) aldehyde. This result is in contrast to that
for acetaldehyde and glycolaldehyde on Zn/Pt(111), where η₂(C,O) bonding of the carbonyl group was observed.

Figure 7.5: HREELS temperature sequence for 0.5 L glyceraldehyde dosed onto a 0.4 ML Zn/Pt(111) surface.

Somewhat surprisingly, little change occurred in the HREEL spectrum upon heating up to 500 K, demonstrating that the surface species present at 300 K remains stable up to this temperature, further emphasizing the stabilization of adsorbed oxygenate intermediates by Zn adatoms on Pt(111). A small ν(CO) peak at 1968 cm⁻¹ from atop bound CO does appear, but this may be mostly due to adsorption of CO from the chamber background. The spectrum obtained at 600 K shows that this temperature was sufficient to induce decomposition of the adsorbed intermediates.
Table 7.2: Vibrational mode assignments for glyceraldehyde on Zn-modified Pt(111)

<table>
<thead>
<tr>
<th>mode</th>
<th>Zn/Pt(111) frequency, cm⁻¹</th>
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<td></td>
<td>200 K</td>
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<td>νOH</td>
<td>3325</td>
</tr>
<tr>
<td>νCH₂, νCH</td>
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</tr>
<tr>
<td>νC=O</td>
<td>1721</td>
</tr>
<tr>
<td>η₁νC=O</td>
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<td>δCH</td>
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</tr>
<tr>
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<td>γCH</td>
<td>718</td>
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<td>δCCO, τOH</td>
<td>632</td>
</tr>
<tr>
<td>νZn-O</td>
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7.3.3 Glucose on Pt(111) and Zn/Pt(111)

TPD data for the reaction of glucose on clean Pt(111), and 0.1 and 0.4 ML Zn/Pt(111) surfaces is displayed in Figure 7.6. As expected, the TPD results for glucose were similar to those for glyceraldehyde. On Pt(111) glucose undergoes decarbonylation/decomposition at relatively low temperatures and the TPD spectra contain desorption-limited CO and H₂ peaks at 414 and 346 K, respectively (Figure 7.6a and b). For the 0.4 ML Zn/Pt(111) surface, the TPD data shows that glucose and glucose-derived intermediates are more stable than on clean Pt(111) as indicated by the presence of higher-temperature CO, H₂ and CO₂ peaks between 550 and 575 K. These higher-temperature desorption peaks, as mentioned above for glyceraldehyde, glycolaldehyde and acetaldehyde, are due to reaction on the bimetallic Zn-Pt sites. The TPD data for the
0.1 ML Zn/Pt(111) surface contain peaks indicative of reaction on both Zn-free portions of the surface and on the bimetallic Zn-Pt sites.

Interestingly, the hydrogen desorption spectra for the 0.4 ML Zn/Pt(111) surface shows some complexity, with three separate peaks at 323, 453, and 571 K (Figure 7.6b) suggesting a stepwise dehydrogenation of the adsorbed intermediates. A small quantity of CH₃OH at 402 K and CH₂O between 400 and 580 K (less than 3 % of the total product yield) were also observed indicating that C-C bond scission occurs in this temperature range.

Figure 7.6: TPD spectra for 0.5 L glucose dosed onto clean Pt(111), 0.1 ML Zn/Pt(111), and 0.4 ML Zn/Pt(111) surfaces. Desorption products include (a) CO, (b) H₂, (c) CO₂, (d) CH₂O, and (e) CH₃OH. Intensity scaling factors relative to the H₂ spectra are indicated in each pane.
A HREELS temperature sequence obtained from Pt(111) dosed with 0.5 L glucose is displayed in Figure 7.7. At 175 K, the spectrum is similar that of glucose adsorbed on Pd(111)\textsuperscript{154} and contains relatively strong ν(OH), ν(C=O), secondary ν(C-OH), and primary ν(C-OH) stretches at 3273, 1600, 1112 and 1055 cm\textsuperscript{-1}, respectively. Complete peak assignments along with comparison data for molecular glucose\textsuperscript{113, 114} and glucose adsorbed on Pd(111)\textsuperscript{154} at 115 K are given in Table 7.3. It is worth noting that previous studies of glucose dosed on Pt(111)\textsuperscript{155} and Pd(111)\textsuperscript{154} have reported that the glucose molecule adsorbs in a ring-open configuration, exposing the aldehyde functionality.

Heating to 200 K sees the emergence of a small ν(C=O) peak at 1736 cm\textsuperscript{-1} in addition to the one at 1600 cm\textsuperscript{-1}. The peak at 1736 cm\textsuperscript{-1} is likely due to a carbonyl group that is not interacting with the surface. The ν(C=O) peak at 1600 cm\textsuperscript{-1}, however, is still present. This peak is within the range expected for both acyl and η\textsubscript{1}(O) carbonyl species, making it difficult to definitively assign. The fact that most aldehydes on Pt(111), including glyceraldehyde, typically undergo C-H bond cleavage to form an acyl intermediate suggests this as the more likely assignment for glucose. Heating the surface to 300 K resulted in little change in the spectrum with the exception of a slight decrease in intensity of the O-H stretching region suggesting the onset of O-H scission. Between 300 and 350 K, unselective C-C and C-H scission occurs producing atop and bridge bound CO (2032 cm\textsuperscript{-1} and 1800 cm\textsuperscript{-1}) and small hydrocarbon fragments.
Table 7.3: Vibrational mode assignments for glucose on various surfaces

<table>
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<th>mode</th>
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<th>Pt(111)$^{15}$</th>
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<td>frequency, cm$^{-1}$</td>
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<td>175 K</td>
<td>200 K</td>
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<td>3339</td>
<td>3619</td>
<td>3270</td>
</tr>
<tr>
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<td>vapor$^{114}$</td>
<td>2944, 2913</td>
<td>2998, 2946</td>
<td>2900, 2876</td>
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<td>$\delta$CH</td>
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</tr>
<tr>
<td>$\rho$CH</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>$\nu$M-C, $\nu$M-O</td>
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</table>

$^{15}$This work. n.r. not resolved.
HREEL spectra as a function of temperature for a 0.4 ML Zn/Pt(111) sample dosed with 0.5 L of glucose are displayed in Figure 7.8. The spectrum at 200 K is similar to that for molecular glucose adsorbed on clean Pt(111) presented above, with peak positions and assignments tabulated in Table 7.3. It is noteworthy that the v(OH) stretch at 3320 cm⁻¹ is quite weak even at 200 K and is almost absent by 300 K. This, in conjunction with the strong v(CO) loss at 1042 cm⁻¹ and v(Zn-O) at 375 cm⁻¹, points to low-temperature O-H scission and formation of Zn-bound alkoxides. Note that a second v(OH) peak is also readily apparent in the spectra at 3545 cm⁻¹. This peak is higher than that expected for glucose and falls in the region that is more appropriately assigned to a Zn-bound surface hydroxyl. We suspect that this peak is due to water adsorbed on Zn. Glucose is highly hygroscopic and thus a small amount of water contamination is unavoidable. While one might initially expect to observe a similar peak for glucose-dosed Pt(111) (Figure 7.7), water interacts only weakly with this surface and desorbs below 170 K. By 400 K significant decomposition of the adsorbed intermediates on the Zn/Pt(111) surface is indicated by the appearance of a strong atop CO peak at 1983 cm⁻¹. Consistent with the TPD data, the HREEL spectra show that decomposition of the adsorbed intermediates is nearly complete by 600 K.

It is also noteworthy that between 200 and 350 K, a v(C=O) stretch at 1725 cm⁻¹ is evident corresponding to a non-surface-interacting carbonyl which is similar to that observed for glucose on Pt(111). This suggests that bonding to the surface via the hydroxyl oxygens competes relative to bonding via the carbonyl group. A small v(C=O) stretch at 1600 cm⁻¹ due to a surface bound carbonyl is still present between 200 and 400
K, however, which again falls in the frequency range consistent with both acyl and η_1(O) species. By comparison to the interaction of the other aldehydes with Zn-modified surfaces we can assign this peak to the η_1(O) species.

Figure 7.8: HREELS temperature sequence for 0.5 L glucose dosed onto a 0.4 ML Zn/Pt(111) surface.

7.4 Discussion

The results obtained in this study of glyceraldehyde and glucose, and those in our previous study of acetaldehyde and glycolaldehyde show that these two sets of molecules follow the same reaction pathway on Pt(111), namely formation of an acyl intermediate.
followed by decarbonylation and unselective C-C, C-H and O-H bond scission to produce CO and H2. In all cases, addition of Zn atoms to the Pt(111) surface increased the stability of the adsorbed aldehydes indicating that the Zn increases the barriers for C-H and C-C bond scission. Note that a similar effect has been reported for Zn-modified Pd(111).61, 62, 64 One effect of the increase in the C-H bond scission barrier was that acyl intermediates were not formed on the Zn/Pt(111) surface and low-temperature decarbonylation did not occur. There was, however, a fundamental difference in the structure of the intermediates formed between the smaller C2 molecules and the larger C3 and C6 molecules. The C2 molecules, acetaldehyde and glycolaldehyde, formed η2(C,O) adsorption complexes in which the oxygen was bound to an oxyphilic Zn site and the C to an adjacent Pt site. This bonding configuration results in a weakened C-O bond in the carbonyl, facilitating carbon-oxygen bond scission. This produces a Zn-bound oxygen that subsequently reacts with adsorbed hydrogen to form an adsorbed hydroxyl group, as evidenced by the v(OH) stretch in the HREEL spectra which emerged upon heating to 400 K. For glycolaldehyde, in addition to the η2(C,O) bonding of the carbonyl group, the alcohol group also underwent dissociation to form an alkoxide. This again was facilitated by the Zn adatoms, with the alkoxide oxygen being anchored to a Zn adatom. C-O scission in the η2(C,O) bound carbonyl similarly occurs, although to a lesser extent than that observed for acetaldehyde.

In contrast to the C2 molecules, the larger aldoses, glyceraldehyde and glucose, were observed to react differently on the Zn/Pt(111) surface. In particular, selective C-O scission in the carbonyl group was not observed for these molecules. The HREELS data
argues against $\eta_2(C,O)$ bonding of the carbonyl which is required for the selective deoxygenation pathway. Instead, an $\eta_1(O)$ bonding configuration of the carbonyl group persists up to 500 K. For these larger aldoses, the HREELS data indicates that adsorption is dominated by O-H scission to form alkoxide intermediates. Also note that, at least in the case of glyceraldehyde, the HREELS data provides evidence for the formation of both primary and secondary alkoxide linkages. This bonding configuration limits the proximity of the aldehyde carbonyl to the surface and precludes the $\eta_2(C,O)$ configuration. It also implies an energetic preference for O-H bond scission and alkoxide formation to $\eta_2(C,O)$ adsorption. This interpretation additionally provides insight into why the extent of selective deoxygenation decreased from acetaldehyde to glycolaldehyde to glyceraldehyde on the Zn-modified surfaces. Furthermore, it extends to the glucose molecule, where no significant surface hydroxyl formation was observed following adsorption, C-O alkoxide stretches dominated the HREEL spectra, and an $\eta_1(O)$ aldehyde was seen to persist up to temperatures as high as 500 K. Because the alkoxide is an apparently more favorable configuration than the $\eta_2(C,O)$ aldehyde, it seems that aldoses with more than one alcohol (glyceraldehyde, glucose) form multiple alkoxide bonds that restrict the proximity of the aldehyde moiety to the surface. This results in species where an $\eta_1(O)$ bond will persist to high temperatures and prevent the $\eta_2$ aldehyde from forming and subsequently deoxygenating, as is the case with glycolaldehyde.
7.5 Conclusions

Based on the results obtained in this study for glyceraldehyde and glucose along with those from our previous study of acetaldehyde and glycolaldehyde, the following conclusions can be drawn: (1) on the Pt(111) surface, all four compounds undergo dehydrogenation at the aldehyde functionality to form an acyl intermediate that subsequently follows a decarbonylation pathway to form CO and H₂; (2) introduction of Zn atoms onto the Pt(111) surface increases the barrier for C-H and C-C bond activation, allowing surface intermediates to persist to much higher temperatures than on Pt(111); (3) on the Zn/Pt(111) surface, alcohol O-H dissociation to form an alkoxide bond(s) competes with adsorption via the aldehyde group, which, in the case of the polyols glyceraldehyde and glucose, precludes the η₂(C,O) bonding of the carbonyl group that is required for selective cleavage of this carbonyl oxygen. This study reinforces the potential for mechanistic control by modifying catalyst properties through alloy effects, particularly Zn-modification of Pt(111), and demonstrates the effect that multiple functionalities in biomass-derived molecules has on the formation and stability of adsorbed intermediates.
Chapter 8. Conclusions

8.1 Summary

The work in this thesis focuses on understanding the catalytic mechanisms of biomass-derived sugars reacting on active noble metal catalysts. Using several surface science techniques including TPD and HREELS, the first studies of glucose adsorption and reaction on Pt(111) and Pd(111) single crystal model catalysts were performed, despite claims of too much molecular complexity. This importantly determined the essential role of the aldehyde function of glucose in its initial adsorption and reaction. Mechanistic studies of complex biomass-derived molecules often require the use of model compounds to simplify the system, and identification of the importance of the aldehyde function in glucose outlined the need to utilize model compounds that have aldehyde functionality in addition to alcohol functionality. Furthermore, using glucose and smaller aldoses as model molecules, reactivity for reforming and deoxygenation chemistry was investigated on Ni-Pd and Zn-Pt bimetallic catalysts. Sub-monolayer adatom Zn deposition on Pt(111) was found to dramatically alter the C-H and C-C bond breaking barriers, allowing surface intermediates to remain intact to much higher temperatures and selective deoxygenation to take place in the smaller aldehydes. These results provide the building blocks for future catalyst design using noble metals in the reactions of biomass-derived compounds, and offer insights into methods for altering bond scission energetics and sequences using bimetallic catalyst constructs.
8.2 Demonstrating the use of Glucose in a Surface Science Study

Chapters 3 and 4 successfully demonstrate the first experimental implementation of glucose in a UHV surface science study by use of a specialized high vacuum effusion chamber shown in Figure 2.5, allowing for the adsorption geometry of glucose on group 10 metals to be elucidated. It was determined that on both Pt(111) and Pd(111) surfaces, glucose initially adsorbs in an $\eta_1(O)$ aldehyde configuration, indicating that not only does glucose ring-open on adsorption, but the aldehyde function is extremely important in the reaction pathway. This supports the conclusion that the smaller molecules used to model glucose and other cellulosic sugars should contain aldehyde functionality in addition to alcohol functionalities. Consequently, this suggests that model aldoses glycolaldehyde and glyceraldehyde are better suited for fundamental study of cellulosic sugars than simple alcohols and polyols like ethanol and ethylene glycol.

8.3 Catalytic Mechanisms for Biomass Reforming

Chapters 3-5 identify the mechanics by which glucose and related model compounds glycolaldehyde and glyceraldehyde react on Pt and Pd catalysts. On both surfaces, at low temperatures, the well defined $\eta_1(O)$ aldehyde energy loss peak at approximately 1715 cm$^{-1}$ paired with the intact hydroxyl (-OH) character indicated that the molecules initially adsorb through the aldehyde function. On Pd(111), it was found that gentle heating resulted in O-H scission and formation of $\alpha$-oxo-$\eta_2(C,O)$ surface intermediates for all three aldoses studied. Further C-C scission with increasing temperature yielded reforming products CO and H$_2$. Addition of Ni to the Pd(111) surface modified this chemistry based on the structure of the surface alloy. TPD yields from Chapter 5 identified that the
reforming activity of Ni-modified Pd(111) surfaces followed the trend Pd(111) > Pd-Ni-Pd(111) ~ Ni-Pd-Pd(111) > thick Ni/Pd(111). This may be a consequence of the fact that the Ni-terminated surfaces were found to produce ethylene at high temperatures, favoring C-O scission over the C-C and C-H scission necessary for the reforming pathway.

8.4 Zn modification of Pt for Hydrodeoxygenation Chemistry
Reactions of acetaldehyde and aldoses glycolaldehyde, glyceraldehyde and glucose on Zn-modified Pt(111) surfaces were investigated using TPD and HREELS in Chapters 6 and 7. It was determined that addition of adatom Zn to the Pt surface significantly decreases C-H and C-C bond scission activity, effectively stabilizing the reactive intermediates. Furthermore, the increased barriers for C-H scission prevent acyl formation (and subsequent decarbonylation) common to aldehyde containing compounds on Pt(111). Instead, Zn stabilizes the $\eta_2$(C,O) configuration of the alloy, preferentially bonding oxygen to the oxyphilic Zn surface atoms. For the smaller molecules acetaldehyde and glycolaldehyde, deoxygenation of the aldehyde oxygen occurred at approximately 400 K. In the larger aldoses, alkoxy formation competed with aldehyde deoxygenation by constraining the bonding configuration of the aldehyde adsorption. Additionally, the differences between electronic alloying effects and site specific geometry were identified in the Zn/Pt(111) systems. Particularly, both forming a near surface PtZn/Pt(111) alloy and creating a sub-monolayer Zn-decorated Pt(111) surface resulted in an electronic effect that decreased C-H and C-C bond scission; however, only when the bimetallic adatom Zn sites were available would adsorbed aldehydes
deoxygenate, indicating a site-specific pathway where aldehyde oxygen atoms bind to oxyphilic surface elements.

8.5 Future Work

As noted in Chapter 1, biomass shows promise as an energy feedstock, touting the ability to produce fuels and chemicals in an environmentally conscious way through the intelligent use of catalysis. The work of this thesis has focused on various catalytic systems for both biomass reforming technology and value added chemical production, particularly in a fundamental capacity. That being said, there is still considerable research that must be done to make biomass an economically competitive feedstock. One route to address the economics is to begin work characterizing biomass chemistry on cheaper catalysts. Investigation of cellulosic sugar reactions on the much cheaper, yet still potentially active and selective carbide family of catalysts will perhaps yield promising results. The work on Ni-modified WC catalysts by Yu et al.47 set the stage for such work, and the screening of other carbides like Mo2C should be of high priority.

Another important vein of study is focus on the production of value added chemicals from feedstocks like furfural and 5-HMF. At the present time, few fundamental surface science studies exist characterizing reactions with 5-HMF due to its difficult vapor pressure window. Accommodations should be made to address this and identify reaction pathways for HDO of 5-HMF on relevant catalysts. Furthermore, facing the important challenge of bridging the pressure and materials gap from fundamental surface science to applied catalyst development is essential. Creating supported mimics of the Zn-Pt bimetallic system studied herein can lead to breakthroughs for physical reactor systems.
Additionally, when using supported catalysts, solvent effects can be investigated, something absent in the UHV studies. Perhaps hydrogen bonding of water during APR dramatically alters the bond breaking energetics, something that should be addressed either theoretically using calculations or using in situ characterization techniques with an APR reactor. Ultimately, the key to developing effective biomass conversion chemistry lies in understanding how catalysts play a role in the reactive mechanisms, and how they can be altered either chemically or structurally to yield more effective technology.
References


(50) Resasco, D. E.; Sitthisa, S.; Faria, J.; Prasomsri, T.; Ruiz, M. P., Furfurals as chemical platform for biofuels production. In Heterogeneous Catalysis in


(69) Suuberg, E. M.; Oja, V.; Lilly, W. D., Vapor Pressures and Heats of Vaporization of Primary Coal Tars. DOE. *Pittsburgh Energy Technology Center*. 1995


