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Mechanistic Studies Of Biomass-Derived Oxygenates Hydrodeoxygenation Reaction Over Bimetallic Catalysts

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Mechanistic Studies Of Biomass-Derived Oxygenates
Hydrodeoxygenation Reaction Over Bimetallic Catalysts

Abstract
There has been a growing interest in converting biomass to value added fuels and chemicals due to the increasing concerns about global warming and sustainable energy. Selective hydrodeoxygenation is an essential step in such conversion. Previous studies have reported that bimetallic catalysts consisting a group 10 metal and a more oxyphilic metal (such as PdFe and PtZn) have efficacy in such upgrading, while fundamental understanding of such reactions is sorely lacking. In this work, a Zn-Pt model catalyst system was used to study the reaction molecules for biomass-derived oxygenates (furfural, benzaldehyde, anisole and guaiacol). Surface science techniques were used provide fundamental insight into the reaction mechanisms as well as the active sites on the catalyst. Overall, it was determined that Zn addition provides a specific binding site for the oxygen atom in the reactant molecule, which helps facilitate the selective C-O bond cleavage reaction. In addition, the interaction between the aromatic ring and catalytic surface is greatly limited by Zn addition, helping to avoid undesired ring saturation. In contrast, the aromatic oxygenates interacts with the Pt(111) surface via the π-orbitals of the ring in a parallel geometry, facilitating ring hydrogenation and unselective decomposition. Such observations were compared with anisole reaction on high surface area supported Pt and PtZn catalysts and consistent results were obtained. To understand how general the effect observed for Zn-Pt system are, reaction of anisole on Co/Pt(111) was also studied. Similar to the Zn addition, Co modifier also interacts closely with the oxygen atom and facilitate selective C-O bond cleavage in anisole. However, a much weaker electronic effect was observed for Co modifier. Similar to the Pt(111) surface, parallel geometry and strong interaction between the ring and Co/Pt(111) was observed.

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MECHANISTIC STUDIES OF BIOMASS-DERIVED OXYGENATES HYDRODEOXYGENATION REACTION OVER BIMETALLIC CATALYSTS

Daming Shi

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ABSTRACT

MECHANISTIC STUDIES OF BIOMASS-DERIVED OXYGENATES
HYDRODEOXYGENATION REACTION OVER BIMETALLIC CATALYSTS

Daming Shi

John M. Voths

There has been a growing interest in converting biomass to value added fuels and chemicals due to the increasing concerns about global warming and sustainable energy. Selective hydrodeoxygenation is an essential step in such conversion. Previous studies have reported that bimetallic catalysts consisting a group 10 metal and a more oxyphilic metal (such as PdFe and PtZn) have efficacy in such upgrading, while fundamental understanding of such reactions is sorely lacking. In this work, a Zn-Pt model catalyst system was used to study the reaction molecules for biomass-derived oxygenates (furfural, benzaldehyde, anisole and guaiacol). Surface science techniques were used provide fundamental insight into the reaction mechanisms as well as the active sites on the catalyst. Overall, it was determined that Zn addition provides a specific binding site for the oxygen atom in the reactant molecule, which helps facilitate the selective C-O bond cleavage reaction. In addition, the interaction between the aromatic ring and catalytic surface is greatly limited by Zn addition, helping to avoid undesired ring saturation. In contrast, the aromatic oxygenates interacts with the Pt(111) surface via the π-orbitals of the ring in a parallel geometry, facilitating ring hydrogenation and unselective decomposition. Such observations were compared with anisole reaction on high surface area supported Pt and PtZn catalysts and consistent results were obtained. To understand how general the effect observed for Zn-Pt system are, reaction of anisole on Co/Pt(111) was also studied. Similar to the Zn addition, Co modifier also interacts closely with the oxygen atom and facilitate selective C-O bond cleavage in anisole. However, a much weaker electronic effect was observed for Co modifier. Similar to the Pt(111) surface, parallel geometry and strong interaction between the ring and Co/Pt(111) was observed.
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Chapter 1  Introduction

1.1 World’s energy consumption and shift of consumption structure

Based on the U.S. Energy Information Administration’s latest International energy outlook for 2017 (IEO2017), the world’s energy consumption increased more than 60% in the past 25 years. Among the various sources of energy, coal and petroleum (and other liquids) contributed more than 55% of the overall increment[1]. While the energy from petroleum and coal contributed significantly to the economic growth in the past, the accompanying pollution, as well as the greenhouse effect led by CO$_2$ emission, has motivated the development of other energy feedstock. The trend to replace traditional fossil fuels with renewable energy sources became especially urgent after signing of the Paris Climate Agreement. To control the future CO$_2$ emission, energy with less or no CO$_2$ would be more preferred.

Based on a recent study, the world’s energy consumption will grow by 28% between 2015 and 2040. As shown in Figure 1.1, it is projected that the future energy consumption will be majorly met by the nuclear, natural gas and renewable (solar, wind, hydro and biomass) energy sources. The traditional energy sources such as coal and petroleum will only contribute 23% of the overall future demand, which dropped significantly compared to 55% for the past 25 years. Meanwhile, the renewable energy is projected to be fastest growing sector, with consumption projected to increase 78% from 2015 and 2040[1], in order to address the increasing concern on the global warming effect.
Comparing with the fast-growing utilization of renewable energy, the consumption for traditional energy sources (coal and petroleum-based energy) will only increase less than 0.4% annually between 2015 and 2040 (~0.7% for petroleum-based and ~0% for coal-based energy. With such reduction in coal and petroleum consumption, it will greatly reduce the emission of CO$_2$ and hence decrease the greenhouse effect) Consequently, dramatic shift in the future energy consumption structure would take place in the near future, as shown in Figure 1.1.

While coal and petroleum serve as a major energy source, the related industries and products are also playing an important role in our daily life. For example, the petrochemicals (like benzene, phenol, and xylene) are important starting materials for plastic, resin, synthetic rubber, etc. The energy consumption structure shift in the future will suppress the use of petroleum, coal and the development of their related industries at the same time. Such structure shift may ultimately lead to the possible shortage of petrochemicals, especially aromatics, which is especially concerning. Take benzene as an example (one of the most important aromatic chemicals, primarily produced from
petroleum or coal processing as a side product); the global demand was estimated at 46 million tons in 2015, with consumption forecasted to grow at an average of 2-3% during 2016-2021 [2]. In contrast, the projected consumption rate for petroleum is less than 0.7%, far below the growth rate for benzene demand. Other chemicals like phenol and xylene are facing a similar challenge. New sources for chemicals, especially the aromatic chemicals, need to be discovered. Fortunately, biomass, as one of the frontrunners of renewable energy sources, stands out as a possible solution for both the demand for green energy and possible new sources for aromatic chemicals.

1.2 Biomass as a feedstock for future energy and chemicals

Biomass is a carbon-based, renewable energy feedstock. In the past, it was commonly utilized via direct combustion. With the development of technology, more and more biomass is converted to various forms of biofuels before used to generate energy to achieve better utilization efficiency. Except for being utilized as an energy feedstock, valuable chemicals can also be developed from such biofuels with further upgrade and separation, making biomass also an attractive source for useful chemicals. The renewable feature makes biomass especially attractive as a future feedstock for energy and chemicals. The ultimate origin of biomass energy comes from the photosynthesis effect of the plant, generating carbonaceous plant from atmospheric CO₂. As a result, any energy or chemical generated from the biomass will lead to no or even negative net carbon release to the atmosphere.

Biomass can generally be categorized into three components, cellulose, hemicellulose and lignin. Cellulose compromise 40-50% of the biomass feedstock [3], is a straight chain polymer of repeating glucose monomer units, linked via a β-1,4 glycosidic linkage, as
shown in Figure 1.2. It is the most ordered component of biomass and can be hydrolyzed to valuable glucose product. Hemicellulose compromises 15-30% of lignocellulosic biomass, is an amorphous branched polymer (Figure 1.2) with a low degree of polymerization (~200). Hence, hemicellulose can be hydrolyzed to yield a mixture of its constituent sugars (such as pentoses and hexose) at a milder condition comparing with cellulose. Lignin makes up the rest of the 15-30% of the biomass weight. Unlike cellulose and hemicellulose, lignin is a highly branched heterogeneous polyphenolic compound (Figure 1.2) with a high degree of aromaticity, making it an attractive feedstock for conversion into value-added fuels and aromatic chemicals.

![Figure 1.2: Schematic representation of the location and structure of lignin in biomass material. (adapted from [3])](image)

When processing the biomass, there is a trade-off between the selectivity and simplicity. When the simplicity of the process is more important, the entire biomass structure can be converted via processes such as gasification or pyrolysis directly, producing hydrogen and bio-oil respectively [3]. Such technology is relevant simple but a large amount of energy is needed. Meanwhile, the valuable functional molecule structure
is destroyed and wasted. With the development of technology, more selective processing can be achieved via chemical, thermal and microbiological process. Each biomass faction (cellulose, hemicellulose, and lignin) can be separated from the overall structure. As a result, more efficient reaction process can be designed and optimized based the unique structure and chemical composition of each biomass fraction to achieve higher selectivity and efficiency. No matter which strategy is preferable, the high oxygen content is the common challenge. Which will lead to low energy density and poor stability for the product.

As mentioned above, two conversion strategies could be applied when trying to upgrade the biomass. Gasification and pyrolysis are usually selected when simplicity is preferred over selectivity of the process, where biomass can be converted in one step without the requirement of fractionation (shown in Figure 1.3). Gasification of biomass can be achieved via high temperature, leading to syngas [4-6]. Fuels could then be produced via a chemical process such as Fischer-Tropsch. Bio-oil, a liquid fuel, could also be produced through pyrolysis [7-10]. However, this low-cost oil consists a mixture of more than 300 chemicals, making it difficult to separate. Meanwhile, the bio-oil contains a high content of water (up to 50%) and many highly oxygenated compounds, leading it to be a poor fuel.
To better utilize biomass as a feedstock for energy and chemicals, a selective route can be achieved via Liquid-Phase reforming. The biomass can be firstly deconstructed using thermal, and/or chemical/catalytic methods to produce functional intermediates (such as the Kraft and Organosoly process) [4, 5, 12-16], which can be then upgraded to a range of end products. The hemicellulose stream can be upgraded to furfural via xylose intermediate (shown in Figure 1.3). The remaining solids, the cellulose fraction of the biomass, can then be hydrolyzed to produce glucose or platform chemicals, such as 5-hydroxymethylfurfural (HMF). Both furfural and HMF are considered as platform molecules with high potential for conversion to a variety of value-added chemicals and fuels [13, 17, 18]. The lignin part can be separated and depolymerized to aromatic intermediates, which can be further developed into value-added fuels and aromatic chemicals [11].

Among the various upgrading routes indicated in Figure 1.3, the liquid-phase reforming process followed by depolymerization is especially valuable for lignin. The
aromatic nature is greatly preserved in such process, which can be then further upgraded to valuable aromatic chemicals. As we mentioned above, benzene is a fundamental starting material for many valuable industrial materials, and a one popular research focus is to produce benzene from lignin [11]. An ideal path is shown in Figure 1.4, by selective depolymerization of lignin, aromatic intermediates could be produced further upgraded to benzene. It is worth noting that, the aromatic intermediates derived from depolymerization of lignin usually have high oxygen content. To further upgrade such intermediates to the valuable product, selective deoxygenation while keeping the aromatic ring intact becomes an essential step.

![Figure 1.4: Ideal reaction pathway for making benzene from lignin](image)

1.3 Bimetallic catalyst in the biomass upgrading

One major challenge in the process to convert biomass to useful fuels and chemicals are the availability of catalysts that are active and selective for the required molecular transformations. In particular, removing the abundant oxygen content in the molecule, while keeping the valuable functional groups (especially the aromatic structure) is a key requirement for such catalyst. Traditional group 10 metal catalysts, such as Pd, Pt, and Ni,
have been explored for such upgrading. Though being active, unfavored ring saturation and cleavage of the useful functional group were also observed, making such catalyst less selective [19-22]. Base metals (e.g., Fe, Cu), on the other hand, was observed with a relatively low activity and not ideal for such reaction as well [22-24]. Alloying the group 10 metal with a more oxyphilic metal (e.g., PtSn, PdZn, and PdFe) has been found to be a promising category of catalysts. Such combination has been shown to greatly increase selectivity while keeping a good activity in the desired upgrading reaction [24-32]. However, there is still lack of understanding in the mechanisms on such catalyst in the corresponding reaction. It is especially important to understand the effect brought by the second metal to the catalyst, and then to build up the connection between the modification of the catalyst and the improved reaction results. Such understanding and correlation would be useful to design better catalyst in the future.

1.4 Upgrading of furfural with bimetallic catalysts

As shown in Figure 1.3, xylose and glucose can be extracted from the biomass, and further processed to furfural and HMF molecules. Furfural is a valuable platform molecule with high potential for fuels and chemicals. It is produced by the hydrolysis and dehydration of xylan within the hemicellulose fraction of biomass. Furfural, as a platform molecule, offers a rich source of derivatives for biofuels, as shown in Figure 1.5. Upgrade for furfural aims to reduce the volatility to blend into diesel or to remove the polarity of the aldehyde group to blend in hydrocarbons. Selective hydrogenation, acid-catalyzed rearrangement or esterification, acid-catalyzed coupling or metal-catalyzed decarbonylation would be needed to achieve such aim.
Among the multiple upgrading routes, removing the oxygen atom in the aldehyde functional group can effectively increase the value of furfural and make it an attractive fuel additive (the process is labeled in blue as shown in Figure 1.5). The product, methyl furan, is with excellent gasoline blending properties and high octane number (high energy density). Ring saturation and decarbonylation reaction need to be prevented in such upgrade as they will either deteriorate the blending property or lower the octane number.

Several studies indicated that the group 10 metals, such as Ni, Pd, and Pt, are not very effective in the upgrading of the furfural. At low temperatures, only hydrogenation activity was reported, producing furfural alcohol with high selectivity [21, 34, 35]. While, at high temperature, decarbonylation reaction dominates, with furan as the major product. Ring hydrogenation and opening were also reported as side products [36]. In a more recent study by Sitthisa et al.[22], it is found that with the addition of Fe to the Ni/SiO₂ catalyst, the selectivity for conversion to methyl furan was greatly increased. Later studies also
indicated that other bimetallic combinations, such as Pd-Fe, Pt-Co systems were also effective in such upgrading[37, 38].

Figure 1.6: Reaction pathways for furfural on Ni and Ni-Fe catalytic surface. (From [39])

Density functional theory (DFT) was applied to elucidate the governing mechanism in the Ni-Fe system by Sitthisa et al. [22]. It was found that the addition of Fe atom on the Ni surface would facilitate a $\eta^2$(C, O) binding configuration, where the oxygen atom would interact strongly with the Fe atom, stretching the C-O bond (weakening it at the same time). As a result, desired C-O bond cleavage achieved while keeping the C-C bond with the furan ring intact (shown in Figure 1.6, top route). While, on the Ni only surface, $\eta^1$(C)-acyl binding configuration is preferred, leading to the undesired decarbonization reaction (shown in Figure 1.6, bottom route). The reaction mechanism proposed by the DFT calculation provides useful insights into the reaction of furfural on the bimetallic catalyst. Since other bimetallic combinations are also reported effective in the furfural upgrading, we are interested if similar reaction mechanism occurred.
1.5 Upgrading of lignin-derived oxygenates with the bimetallic catalyst

As mentioned in the above sections, there is an increasing interest in converting the lignin part of biomass into fuels and chemicals. The aromatic nature of lignin makes it especially attractive to achieve the conversion from lignin to the aromatic chemicals.

As shown in Figure 1.3, depolymerization of lignin via fast pyrolysis or other means produces a range of oxygenated aromatics with phenol, anisole, benzaldehyde, salicylaldehyde, and guaiacol as typical examples [11, 40-43]. The high oxygen content in many of these molecules is problematic since it reduces their stability and suitability as a feedstock for fine chemicals. Thus, upgrading by partial or complete oxygen removal is likely to be necessary for any commercial process using lignin as a starting material. Such requirement has motivated studies of the catalytic deoxygenation of lignin-derived molecules [3, 11]. Several studies of the use of supported group 10 metal catalysts (Ni, Pt, and Pd) for this purpose have recently appeared in the literature [24, 44-47]. These monometallic catalysts, however, are not highly selective for deoxygenation and tend to promote the undesired hydrogenation of the phenyl rings resulting in non-aromatic products. Base metal, on the other hand, has also been applied in upgrading lignin-derived oxygenates. While selective results were observed, the overall reactivity was reported to be lower compared with the group 10 metal [24, 48]. Bimetallic catalysts composed of a group 10 metal alloying with a more oxyphilic metal, such as Co, Sn, or Zn, have been reported with ideal activity and selectivity, with oxygen removal achieved without ring hydrogenation [3, 24-26, 43, 48-52].
One study on the upgrading of guaiacol with Pd-Fe bimetallic catalyst serves as a great example [24]. It was found that a 2 wt% Pd-10wt% Fe on carbon catalyst had significantly improved yield of oxygen-free products during guaiacol deoxygenation compared to both 10 wt% Fe/C and 5 wt% Pd/C, with the yield of benzene plus toluene for these catalysts being 25.9%, 6.3% and 2.7%, respectively at 350°C (0.4 kPa guaiacol, 40 kPa H₂). The reaction pathways observed for base metal (Fe, Cu), bimetallic (Pd-Fe) and noble metal (Pd, Pt, Ru) catalysts are shown in Figure 1.7. Characterization studies revealed that the surface of the Pd-Fe alloy was highly enriched in Pd, but the mechanism by which promoting the enhanced performance was not revealed. Similarly, other bimetallic catalysts such as Zn-Pd, Sn-Pt were also reported to be effective in upgrading guaiacol or other lignin-derived oxygenates [25, 26], but the insight into both the mechanisms and active sites for these reactions and the nature of the synergistic interactions between the two components of the bimetallic are sorely lacking [3, 53].

![Figure 1.7: Reaction pathways for the deoxygenation of guaiacol on Pd, Pt, and Ru (blue) and Cu, Fe, and Pd-Fe (red). (adapted from [24])]
1.6 Thesis objectives

Based on the studies mentioned above, it can be concluded that group 10 metal possess a high hydrogenolysis activity. While making it highly active in the desired C-O bond cleavage in the deoxygenation reaction, such property also promotes the unfavored ring hydrogenation in the biomass-derived oxygenates upgrading, making it less selective to become an ideal catalyst for such reaction. The base metal, on the other hand, is not ideal for the biomass upgrading due to its low activity. The bimetallic catalyst, via alloying the group 10 metal with a more oxyphilic metal, greatly increased the selectivity while keeping a high activity, making it a great candidate for biomass upgrading catalyst.

The overall goal of my research was to provide a fundamental insight into what controls the activity and selectivity of such bimetallic catalysts, with the focus on identifying the specific active sites for C-O bond cleavage and understanding how the alloying contributes to the decreased ring hydrogenation activity. Specific questions that were the focus of my thesis research are as follows:

1. Will other bimetallic combination (a group 10 metal and a more oxyphilic metal, e.g., Pt-Zn, Pd-Co) exhibit similar selectivity and chemistry as furfural on Ni-Fe catalyst?
2. How will other oxygen-containing functional groups (such as the -OH and O-CH₃) interact with the bimetallic catalytic surface? Will a η²(C, O) bonding configuration be formed for other oxygen-containing functional groups? If so, will such binding configuration also play a key role in the C-O bond cleavage?
3. Will alloying affect the interaction between the aromatic ring and the catalytic surface? Can we control the strength of the ring-surface interaction by different metal combinations?

4. Will the presence of multiple functional groups (-OH, -O-R, -CHO) in the biomass-derived oxygenate lead to different binding configuration and consequently different chemistry on the bimetallic catalyst?

Answering these questions will provide useful insights to achieve a better understanding on the biomass-derived oxygenates upgrading. It will also help to bridge the enhanced performance of the bimetallic catalyst to its modification, giving guidance for the design of highly-active and selective bimetallic catalysts for the upgrading of biomass in the future.

1.7 Surface science for bimetallic catalyst in biomass upgrading

Though extensive studies on high surface area supported catalysts have reported that, bimetallic catalyst consisting a group 10 metal and an oxyphilic metal are effective in the HDO upgrading of biomass derived oxygenates[3, 22, 24-27, 43, 48-52, 54], the understanding on the reaction mechanism and role of different metals in the reaction are sorely lacking. Traditional reactor studies fall short in identifying the specific reaction intermediate and characterizing the structure of the high surface area catalyst. Model single crystal catalyst was therefore used, whose surface can be well controlled, and the reaction on such surface is studies with a range of surface science technique to develop the understanding of the reaction mechanism and active catalytic sites involved. With the help of ultra-high vacuum system, powerful surface science techniques such as high-resolution electron energy loss spectroscopy (HREELS) and x-ray photoelectron spectroscopy (XPS)
can be used to study model reagent molecule reaction on the model catalytic surface. Detailed molecule bonding configuration, active reaction site as well as corresponding reaction pathway could be revealed; such detail is normally inaccessible in regular reactor studies.

A study on the hydrodeoxygenation on cellulose-derived oxygenates by our group served as a great example, demonstrating the power of surface science techniques in understanding the reaction mechanism as well as the roles of the different metals on the surface[39]. To illustrate the level of detail we can achieve by such approach, a portion of the previous study is briefly summarized below.

Acetaldehyde is selected as a model molecule for the cellulose-derived oxygenate. TPD experiment was performed on Pt(111) and Zn/Pt(111) surfaces with various Zn coverage. Based on the TPD data shown in Figure 1.8, CO and H$_2$ are the major products from all surfaces. On the clean Pt(111) surface, large desorption-limited CO and H$_2$ peaks are observed at 406 and 332 K respectively, suggesting complete dehydrogenation and C-C bond cleavage occurred below room temperature. When alloying the Pt surface with Zn, a significant fraction of the glycolaldehyde desorbs intact at 164 K, indicating a large decrease in the activity. By our previous study, Zn is located in the second and third layers in the model surface[55], indicating the electronic effect is the major cause of for the decreased activity.
Figure 1.8: TPD data for the reaction of acetaldehyde on Pt(111), PtZn/Pt(111), and Zn/Pt(111) surfaces.

Except for the TPD data, the vibrational spectra of the adsorbed intermediates can bring more insight in the reaction pathway and the active catalytic sites for the reaction. HREEL spectra of Pt(111) and Zn/Pt(111) (Zn present as adatoms) dosed with 0.5 L of acetaldehyde at 115 K are displayed in Figure 1.9 below. Acetaldehyde undergoes C–H bond cleavage to form acetyl by 200 K on Pt(111), suggested by the appearance of ν_{acetyl}(C=O) stretch at 1580 cm⁻¹. With further increase of the temperature, surface intermediate undergoes decarbonylation yielding CO, as indicated by the atop CO ν(C=O) stretches at 2055 cm⁻¹.

Figure 1.9: HREEL spectra as a function of temperature for acetaldehyde-dosed (a) Pt(111) and (b) 0.5 ML Zn/Pt(111)
Instead of forming acyl (RC=O) intermediate on Pt(111) surface, the acetaldehyde would interact with the Zn/Pt(111) surface via the aldehyde group in a $\eta^1$(O) configuration at low temperatures (bonding via the aldehyde oxygen), as indicated by the $\nu_{\text{aldehyde}}$(C=O) stretch at 1680 cm$^{-1}$ in the HREEL spectra at 200 K. With increase of the surface temperature, a $\eta^2$(C, O) configuration is formed, where both the oxygen and the carbon in the carbonyl group interact with the surface. Such surface intermediate is stable up to 400 K, at which point the C-O bond cleavage in the $\eta^2$(C, O) aldehyde occurs, resulting in the formation of adsorbed surface hydroxyls signified by the appearance of a $\nu$(OH) stretch at 3575 cm$^{-1}$ for acetaldehyde. In our paper [56], multiple surface science techniques, such as HREELS, XPS, and AES, are applied and demonstrated that the formation of the $\eta^2$(C, O) intermediate occurs through the interaction between the carbonyl oxygen and an oxyphilic Zn atom. Such binding configuration would result in weakening the C=O bond in the reaction intermediate, leading to C-O bond cleavage. A schematic showing the proposed reaction pathways and stable intermediate is shown in Figure 1.10.

![Figure 1.10: Proposed pathways and intermediates for the adsorption and reaction of acetaldehyde on Zn/Pt(111) adatom surfaces. (adopted from [56])](image)

In our study above, we demonstrated the reaction pathway of acetaldehyde on the Pt(111) and Zn/Pt(111) surface. The binding configuration, the roles of different metals on
the surface, and the structure of key reaction intermediate are all revealed with the help of
the powerful surface science technique. Though the biomass-derived oxygenates have a
much more complex molecule structure because of the aromatic ring, the surface science
technique will still play an important role in the following way:

1. Understand the catalytic activity of the target mono- and bimetallic catalyst with
   the help of TPD technique in a similar way as our study in acetaldehyde mentioned
   above

2. Understand the interaction between the key functional groups (-OH, -O-R, -CHO)
   and the catalytic surface with the help of HREELS technique. When a chemical
   bond or a strong interaction formed between the functional groups and the metal
   surface, the emergence of a specific vibrational peak will be observed in the
   HREELS data

3. Understand the molecule structure of the key reaction intermediate with the help of
   the HREELS and TPD data

The study on the model aldehyde molecules on Zn-Pt surface is a great starting point,
future studies on furfural and benzaldehyde (a lignin-derived oxygenate) can be developed
based on it. Though the interaction between the aldehyde functional group and the catalytic
surface is well studied, the role of the aromatic ring in such reaction needs to be
investigated. Other than furfural and benzaldehyde, studies on reaction of other lignin-
derived oxygenate on different bimetallic surface can be developed with the help of surface
science techniques as well.
1.8 Thesis scope

This thesis is divided into 8 chapters. Chapter 2 provides an explanation of the research apparatus and the experiment methods used in the studies. Chapter 3 demonstrates the effectiveness of Zn-Pt bimetallic catalyst for the upgrading of cellulose-derived oxygenate, furfural. This study provides useful insight of the reaction mechanism on such catalytic surface, also reveals the potential of such bimetallic in upgrading of lignin-derived oxygenates. Chapter 4 and Chapter 5 identified the reaction mechanism of lignin-derived oxygenates (benzaldehyde and anisole) on the Pt and Zn/Pt surface, effective HDO reactivity is observed for both molecules. Chapter 6 reveals the potential for Zn/Pt bimetallic in facilitating HDO reaction of guaiacol, which is a lignin-derived oxygenates containing two functional groups. Chapter 7 expands the study of Chapter 5, and reveals reaction pathway of anisole on Co/Pt. Chapter 8 will summarize the major conclusions drawn within each of the major sections of the thesis.
Chapter 2 Experimental

2.1 Introduction

As mentioned in the introduction chapter, extensive studies indicated bimetallic metal catalyst, especially the combination of a group 10 metal and a more oxyphilic metal such as PtZn and PdFe, demonstrated excellent efficacy in the desired HDO upgrading for biomass. However, the fundamental understanding of the relationships between the catalyst structure, composition, and reactivity are difficult to discern when using high surface area supported metal catalysts. The heterogeneous nature of these catalysts results in there being a range of surface features and active sites, making it difficult to identify the specific active sites of the catalyst, the reaction pathways, as well as the synergistic effect of the two metals, etc. To overcome these limitations and develop detailed structure-activity relationships in this thesis project surface science techniques were utilized to study the HDO reactions of model biomass-derived oxygenations on well-defined single-crystal model catalytic surfaces, such as the Pt(111) and the Zn modified Pt(111). With the help of a range of surface sensitive spectroscopic techniques, the bonding configuration of the surface species, the reaction mechanism as well as the active sites of the catalyst could be characterized and identified specifically.

Throughout the thesis, Pt(111) surface and two well-characterized bimetallic surfaces, Zn-Pt and Co-Pt, were utilized to study the reaction of biomass-derived oxygenates, such as furfural, anisole and benzaldehyde. Most of the experiments were conducted in an ultra-high vacuum (UHV) surface analysis chamber with a base pressure of $2 \times 10^{-10}$ Torr, equipped with various spectroscopic instruments such as TPD and HREELS. A liquid phase flow reactor was also utilized to compare the reactivity of Zn-Pt model catalysts and
high surface area catalysts. This chapter describes the UHV surface analysis chamber, sample preparation, the surface characterization techniques, and the flow reactor setup used throughout the thesis study.

2.2 Surface analysis techniques

2.2.1 Temperature programmed desorption (TPD)

In the research reported here temperature programmed desorption (TPD) was used as the primary technique to characterize the adsorption and reaction of biomass-derived oxygenates on model catalytic surfaces. TPD, also referred to as thermal desorption spectroscopy, 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. In a TPD experiment a surface of interest (mono- or bimetallic surface) is exposed to a reactant molecule allowing it to adsorb on the surface. After the desired amount of reactant molecules are dosed, the temperature of the surface is ramped up linearly while a mass spectrometer, positioned in front of the sample surface, is used to monitor the identity of desorption products (shown in Figure 2.1).
TPD experiments will help to monitor the energetics of the catalytic surface, adsorption interactions and surface reaction pathway. Before we start to analyze a sample TPD data, it is instructive to identify the theory behind. The rate of desorption can be described in the following equation

\[-\frac{dN}{dt} = k_d N^m\]  \hspace{1cm} \text{Equation 2.1}

\(N\) is the number of molecules adsorbed on the surface, \(m\) is the order of reaction and \(k_d\) is the desorption rate constant, which is defined by the following equation.

\[k_d = A \cdot e^{-E_d/RT}\]  \hspace{1cm} \text{Equation 2.2}
A is the pre-exponential constant factor, $E_d$ is the activation energy for desorption and $T$ is the absolute temperature. Since the heating rate is linear in time while performing TPD, $\frac{dT}{dt}$ would be a constant $\beta$. By rearranging Equation 2.1 and plug in Equation 2.2, the following Equation 2.3 could be achieved.

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

Equation 2.3

If we take the H$_2$ peak at 340 K in Figure 2.2 as an example. The $\frac{dN}{dT}$ term will be zero at $T_p$ (temperature for desorption peak maximum, around 340 K), the activation energy of the reaction can then be derived via following equation:

$$\frac{E_d}{RT_p} = \frac{A}{\beta} e^{-E_d/RT_p}$$

Equation 2.4

A further simplified equation to determine the activation energy can be achieved with the assumption that the activation parameters are independent of surface coverage and the desorption kinetics are first order, which is known as Redhead Equation:

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

Except the activation energy, the initial surface coverage can also be derived from the TPD data, which requires calibration to a known reagent and subtraction of background adsorption.
To have better understanding of the TPD technique, a typical TPD experiment of diethyl ether reaction on Pt(111) is plotted in Figure 2.2 as an example. A zeroth order diethyl ether desorption peak was observed at 220 K, corresponding to the physisorbed multilayer-adsorbents. Large desorption-limited H\textsubscript{2} and CO peaks observed at 340 and 465 K respectively, suggesting dehydrogenation and C-C bond cleavage occurred at lower temperature range. A series of reaction-limited H\textsubscript{2} peaks were observed spanning between 400 and 600 K, indicating further dehydrogenation of the surface hydrocarbon species.

2.2.2 High resolution electron energy loss spectrometry (HREELS)

Though a rich and informative technique, TPD provides limited insight into the identity of stable reactive intermediates that are adsorbed on the catalyst active sites. More
detailed insight can be obtained from a surface sensitive vibrational spectroscopy, such as HREELS. HREELS operates in a similar way as infrared (IR) or Raman spectroscopy. Instead of photons, low-energy electrons are employed in the technique, making it an effective surface specific technique to study adsorbates on the catalytic surface. HREELS works under the principle that molecular vibrations (such as wags, torsions, deformations, rocking, etc.) excite in quantized energies characteristic of their molecular composition and bonding configuration, the surface-bound intermediates can therefore be identified based on their characteristic vibrational spectra.

HREELS utilizes the inelastic scattering of low-energy electrons to measure vibrational spectra of surface species: superficially, it can be considered as the electron-analogue of Raman spectroscopy. A monochromatic electron beam is directed at the surface of interest. Though most electrons will reflect elastically off the sample into the detector, any surface species having a dynamic dipole moment oriented perpendicular to the surface can be excited to a higher vibrational state, resulting in a quantized loss of energy in the electron that is manifested as a peak in the energy loss spectrum. Analyzing the peak location in the HREEL spectrum, useful information about the chemical structure of the surface species could be achieved.
Figure 2.3: Schematic of HREEL spectroscopic principle, with a mono-energetic collimated electron beam at energy $\varepsilon$ introduced to the catalytic surface. (a) electron beam reflects elastically at no loss of energy and forming a (b) elastic peak in HREEL spectrum. (c) electron beam interacts with a surface species dipole, exciting the molecular vibration to the next energy level at $\delta$ above the ground state, resulting in a reflection with $\varepsilon$ energy loss, forming (d) a corresponding HREEL spectrum from the reflection with $\varepsilon$ energy loss.

In addition to identifying the chemical structure, HREELS data can also provide useful information about the bonding configuration of the surface species. As described above, the transfer of energy between the incident electron and the adsorbed dipole leads to the peak in the HREEL spectrum. Hence, the intensity of the peak is determined by the strength of the molecular dipole. Meanwhile, the orientation of the dipole with respect to the surface is also playing an important role in the peak intensity in the spectrum. For the molecular dipole perpendicular to the surface, the intensity of the corresponding peak will be reinforced by the induced dipole image in the metal surface. While, the intensity for parallel molecular dipoles are damped out by the induced dipole image (see Figure 2.4). Based on the peak location and its relative intensity information, the structure of the surface species together with its binding configuration could then be derived, which makes HREELS a powerful technique to understand the mechanistic of reactions on the catalytic surface.
2.3 Ultra-High vacuum surface analysis systems

As mentioned in the above section, TPD and HREELS techniques are two powerful surface science techniques to study the reaction occurred on the catalytic surface. And to utilize such powerful surface spectroscopy, it is necessary to make sure the mean free path of probe and detected particles (atoms, electrons, etc.) in the system must be significantly greater than the dimensions of the analysis apparatus. Mean free path is defined as below:

$$\lambda = \frac{kT}{1.414P\sigma}$$

P is the pressure, k is the Boltzmann constant, T is the temperature and \(\sigma\) is the collision cross section. Hence a low pressure (usually \(\sim 10^{-5}\) Torr) is required for such techniques.

In addition, to begin experiments with a reproducibly clean surface and to avoid any significant contamination by background gaseous during the experiment, the operating pressure must be low enough (UHV condition) that the time required for contamination build-up is substantially greater than that required to conduct the experiment. To further
illustrate the improtance of the vacuum environemnt, a brief calculation will be conducted to show how the UHV condition limits the interaction between a catalytic surface atom and a surrounding gaseous molecule comparing with atmospheric pressure.

Based on the kinetic theory of gases, the equation for collision frequency of gas molecules with a surface is stated as below,

\[ \phi = \frac{1}{4} n v_{rms} \]  
Equation 2.5

\( \Phi \) is the collision rate, which is the number of collisions a surface to experience per unit time per unit per unit area. \( n \) in the equation is the number of molecules per unit volume. And \( v_{rms} \) is the average (root mean square) speed of the gas molecules, and it is defiend in the equation below:

\[ v_{rms} = \sqrt{\frac{3K_bT}{M_m}} \]  
Equation 2.6

\( K_b \) is the Boltzmann constant, \( T \) is the absolute temperature and \( M_m \) is the molar mass of the gas particles.

After combining , Equation 2.5 and 2.6, the following Equation 2.7 can be obtained. \( R \) is the ideal gas constant, \( P \) is the pressure, \( MW \) is the molecular weight, and \( N_A \) is the Avogadro’s number. The collision frequency could then be detemined by the molecular weight of the gas particles, and the temperature and pressure of the environment around the catalytic surface.

\[ \phi = \frac{3N_A}{R} \frac{P}{4 \sqrt{MW \cdot T}} \]  
Equation 2.7
For the UHV condition, the base pressure is approximately $2 \times 10^{-10}$ Torr. Assume the experiment is conducted at room temperature (298 K) and surrounded by N$_2$ molecules ($MW$ is 28). Plug in those parameters into Equation 2.3 and we can have the following result:

$$\Phi (298 \text{ K}, 2 \times 10^{-10} \text{ Torr}) = 8.4 \times 10^{10} \text{ cm}^{-2} \text{s}^{-1}$$

On a typical catalytic surface, such as Pt(111) crystal, there are approximately $1.51 \times 10^{15}$ Pt atoms per cm$^2$. The time between two collisions for each atom on the surface is about 18,000 seconds, or 5 hours. On the other hand, if the same surface is placed at the same temperature and surrounded with N$_2$ molecules, but at atmospheric pressure environment (~760 Torr), the corresponding collision frequency would be:

$$\Phi (298 \text{ K}, 760 \text{ Torr}) = 3.2 \times 10^{23} \text{ cm}^{-2} \text{s}^{-1} = 2.1 \times 10^8 \text{ s}^{-1} \text{ (per Pt atom)}$$

In other words, each Pt atom will experience approximately 200 million collisions with the surrounding gas N$_2$ molecules per second. Therefore, the UHV condition would greatly avoid the possible influence brought by the environment gaseous molecules, allowing us enough time to focus on the target reaction.

In our group, the experiments of interest were conducted under the UHV condition enabled by a chamber apparatus as shown in Figure 2.5. The UHV condition within the chamber was achieved via a 3-stage pumping process. The chamber’s pressure could be pumped down to $10^{-5}$ Torr by a mechanical rotary vane roughing pump. The second stage of vacuum, which is up to $10^{-8}$ to $10^{-9}$ Torr, is achieved by a turbomolecular pump. The last stage of the vacuum condition, is brought by an ion pump at the bottom of the chamber and the target pressure, $2 \times 10^{-10}$ Torr, would be achieved.
With the help of the UHV system, catalyst preparation and analysis could be performed. At the top chamber section, the single metal crystal sample could be cleaned with Ar⁺ ion bombardment facilitated by a PHI electronics sputter gun. If a bimetallic surface is desired, a second metal could also be introduced via a metal deposition feedthrough, with the deposition amount monitored via a quartz crystal microbalance (QCM). When a desired catalytic surface is prepared, it could then be exposed to reactant molecules controlled by a variable leak valve to study the corresponding reaction. An SRS RGA200 quadrupole mass spectrometer is also mounted at the top part of the chamber to study the reaction occurred on the catalytic surface. At the lower section of the chamber, a HREEL spectrometer from LK technologies is installed on the chamber to obtain useful vibrational spectra from the catalytic surface.
2.4 Sample preparation

2.4.1 Monometallic surface preparation

In the studies throughout the thesis, a Pt(111) single crystal and Pt(111) modified by a second metal were utilized as model mono- and bimetallic catalytic surfaces respectively. A Pt(111) single crystal substrate (Goodfellow), with 5N purity, 1 cm diameter and 2mm thick served as the model catalyst. Before being mounted into the chamber, the sample was mechanically polished with diamond paste from 15 μ to 0.5 μ in dimension in order to achieve a mirror finish on one side of the sample.

After mechanical polishing, the crystal was then mounted and put into the chamber. To further clean the sample and achieve a perfect Pt(111) surface structure, annealing and Ar\(^+\) ion bombardment were used. Repeated cycles as described below are needed:

i) 2 kV Ar\(^+\) bombardment via the PHI sputter gun for 40 min, operated under Ar pressure at 5x10\(^{-6}\) Torr)

ii) Annealing at 1100 K in 10x10\(^{-8}\) Torr of O\(_2\) for 15 min

iii) Annealing at 1100 K at vacuum for 10 min (~2 × 10\(^{-10}\) Torr)

In such process, the top layer impurities on the surface would be cleaned via the bombardment damage by Ar\(^+\); annealing under O\(_2\) would facilitate to oxidize the impurities and further clean the surface; annealing the surface at high temperature would restructure the surface back to (111) structure. After approximately 6-10 cycles of sputtering and annealing, an ideal Pt(111) catalytic surface structure would be ready for our study.
2.4.2 Bimetallic surface preparation

For desired bimetallic catalytic surface, such as the Zn-decorated Pt(111) surface, a second metal needed to be introduced to the Pt(111) surface. Preparation of such bimetallic surface was enabled via the use of an evaporative metal source which is heated by a tungsten or tantalum filament. While depositing the second metal, the sample Pt(111) surface will be positioned facing the metal flux generated from the source, which is monitored by the quartz crystal microbalance (QCM) situated in plane with the catalyst crystal as shown in the Figure 2.6.

Figure 2.6: Schematic of the metal deposition configuration

As will be discussed further in later chapters, different surface structures could be prepared based on different methodology. Taking the Zn-Pt bimetallic surface as an example, two general bimetallic forms were produced. The first is a Zn/Pt(111) structure,
where the Pt surface is decorated by Zn ordered adatoms over-layer. Such structure is formed by depositing Zn on to the Pt(111) surface at room temperature or cooler. If the adatom Zn/Pt(111) surface was then annealed to 600 K for 2 min, a near-surface PtZn/Pt(111) alloy would be formed. The different Zn-Pt structures were well characterized via X-ray photoelectron spectroscopy [57]. As shown in in the Figure 2.7, the XPS data of Zn(2P\textsubscript{1/2}) obtained on the 0.2 ML Zn/Pt(111) surface annealed progressively to higher temperature. When the temperature is below 450 K, the Zn(2P\textsubscript{1/2}) binding energy was 1044.8 eV, which is consistent with that reported previously for Zn adatoms on the Pt(111) surface. When annealing the surface to 500 K and above, decrease in the Zn(2P\textsubscript{1/2}) binding energy was observed, indicating the incorporation of adsorbed Zn atoms into the Pt(111) surface to form a PtZn alloy.
Figure 2.7: Zn(2p$^{1/2}$) XP-spectra of 0.2 ML Zn/Pt(111) samples annealed progressively to higher temperature (from [57])

2.5 High surface area catalyst study - three-phase flow reactor system

To bridge the observations obtained from the model catalytic surface with the results obtained from high surface area catalyst, a three-phase flow reactor system (as shown in the Figure 2.8 below) similar to that was described by Luo et al. [58] was utilized in this thesis.
Figure 2.8: Diagram of the three-phase continuous flow reactor (adopted from [58])

The reactor is a stainless-steel tube, 20-cm long, with a 4.6-mm ID, which is heated in a tube furnace. The reactant solution liquid feed is introduced to the reactor via a High-performance liquid chromatography (HPLC) pump (Series I+, Scientific Systems Inc.), which is also used to measure the total pressure in the reactor. Meanwhile, the \( \text{H}_2 \) (UHP grade, Airgas) flow was fed to the reactor and controlled by varying the pressure drop across 8 feet of 0.002-inch ID capillary tubing (Valco Instruments, Inc.). The pressure within the reactor was controlled by a back-pressure regulator (KPB series, Swagelok) placed at the reactor exit. The liquid flow rate could be varied from 0.02 to 0.2 mL/min by the HPLC pump, while the \( \text{H}_2 \) flow could be varied from 2 to 20 mL/min controlled by the back-pressure regulator. Since the products left the reactor at room temperature, product analysis was carried out using a syringe to inject the liquid effluent into a GC-MS (QP-5000, Shimadzu), equipped with a capillary column (HP-Innowax, Agilent Technologies). Detailed reactor setup and the experimental condition will be discussed in the later chapters.
Chapter 3 Deoxygenation of Biomass-Derived Oxygenates: Reaction of Furfural on Zn-Modified Pt(111)¹

Summary

Temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) were used to characterize the adsorption and reaction of furfural on Pt(111) and Zn-modified Pt(111) surfaces. Furfural was found to bond to Pt(111) via the aromatic ring which facilitated C-C bond scission and ring opening at low temperatures leading to unselective decomposition to CO and H₂. In contrast on Zn-modified Pt(111), furfural bonds via the aldehyde carbonyl in an η₂(C,O) configuration with the aromatic furan ring tilted away from the surface. This bonding configuration weakens the C-O bond in the carbonyl which undergoes scission upon heating above 250 K to form a stable (C₄H₃O)-CH= intermediate. These results provide useful mechanistic insights for the hydrodeoxygenation of furfural on PtZn catalysts.

¹ This chapter was published as Shi, Daming, and John M. Vohs. Acs Catalysis 5.4 (2015): 2177-2183.
3.1 Introduction

The desire to produce fuels and chemicals by more sustainable and environmentally sympathetic methods has motivated research on the use of cellulosic biomass as a feedstock. [16, 59, 60] The effective utilization of this renewable resource, however, requires the development of efficient chemical pathways and catalysts for the conversion of biomass-derived molecules into more useful products. Due to the high oxygen content in the constituent C$_6$ and C$_5$ sugars in cellulose and hemicellulose, at least some deoxygenation is generally required. Hydrodeoxygenation (HDO) of furfurals, which are produced from the dehydration of the sugars, in particular, is a key step in many of the reaction pathways proposed for the upgrading of cellulosic biomass into value added fuels and chemicals. [13] Traditional metal catalysts that have high hydrogenolysis activity, such as Ni and Pd [21, 34, 36], have been explored for these HDO reactions, but they tend to promote either undesirable decarbonylation that results in a decrease in carbon number or hydrogenation of the aromatic ring.

Several studies in the literature have reported that the decarbonylation activity can be suppressed by alloying a group 10 metal with a second more oxyphilic metal. [22, 54, 61] For example, Sitthisa et al. [22] have reported that for typical HDO conditions, reaction of furfural on supported Ni produces primarily decarbonylation products. Alloying the Ni with Fe, however, dramatically shifts the selectivity to the desired 2-methylfuran HDO product. Another interesting aspect of this study is that hydrogenolysis of the aldehyde carbonyl over Ni-Fe catalysts occurs without hydrogenation or opening of the aromatic furan ring which would be expected on Ni alone. [62] Similar results have also been reported for the HDO of lignin-derived aromatic oxygenates where alloying a group 10
metal with a more oxyphilic metal (e.g. PtSn, PdZn, and PdFe) enhances both HDO selectivity while simultaneously inhibiting the activity for aromatic ring hydrogenation.[25, 26]

To provide insight into how alloying alters the activity and selectivity of this class of catalysts, we have recently been studying the reaction of aldehydes and aldoses, including glucose, on model catalysts consisting of Zn-modified Pt(111) and Pd(111) surfaces.[39, 63, 64] For the reaction of simple aldehydes, such as acetaldehyde and glycolaldehyde, on Pt(111) it was observed that adding small amounts of Zn to the surface suppressed formation of acyl intermediates which readily undergo decarbonylation, and stabilized an $\eta^2$(C,O) configuration of the aldehyde carbonyl in which the O is bonded to a Zn site and the C to a Pt site. This bonding configuration results in a weakening of the C-O bond which facilitates its cleavage.[39] These experimental results are consistent with DFT calculations for similar reactions on Ni and NiFe surfaces reported by Sitthisa et al.[22]

In the work reported here we have expanded our previous temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) studies of the reaction of aldehydes on Zn-modified Pt(111) to include the reaction of furfural on this surface. The goal of the study was to determine how Zn addition to Pt alters the bonding of both the carbonyl and aromatic furan ring to the surface and to identify stable reaction intermediates that are involved in the HDO of furfural on PtZn catalysts.
3.2 Experimental

All experiments in this study were conducted in an ultrahigh vacuum (UHV) apparatus which has been described in previous publications.[39, 63-65] The system was operated with a 2×10^{-10} torr background pressure, equipped with an SRS RGA200 quadruple mass spectrometer, an ion sputter gun (PHI electronics) and an HREEL spectrometer (LK Technologies). The Pt(111) single crystal substrate was 10 mm in diameter and oriented to within ±0.5°. The Pt crystal was spot-welded to two tantalum wires that were connected to UHV sample manipulator and could be heated resistively and cooled to 115 K by conduction from a liquid N\textsubscript{2} reservoir. The sample was cleaned by repeated cycles of 2 kV Ar\textsuperscript{+} ion bombardment at 600 K for 30 min, annealing at 1200 K in vacuum for 15 min, and annealing at 1200 K in 2×10^{-8} torr O\textsubscript{2} for 15 min.

The furfural reactant (Sigma Aldrich, 99%) was contained in a glass vial that was attached to a stainless steel manifold that was connected to the main UHV apparatus via a variable leak valve. A 3 K/s heating rate was used in all TPD experiments. A series of TPD experiments on Pt(111) showed that saturation coverage in the first monolayer occurred for a 0.6 L furfural dose at 115 K. For this reason a 0.6 L furfural dose was used in the TPD experiments reported below.

HREEL spectra were collected using a 4 eV electron beam oriented at 60° with respect to the surface normal. The full width at half-maximum of the elastic peak on the clean surface was typically 40 cm\textsuperscript{-1}. HREEL spectra were collected as a function of sample temperature. For temperatures greater than the dosing temperature the sample was heated at 3 K/s to the indicated temperature and then rapidly quenched to low temperature at which point the spectrum was collected.
Zn-modified surfaces were prepared by exposing the Pt(111) surface to a beam of Zn atoms produced using a thermal evaporative source that consisted of a small coil of Zn wire (Alfa Aesa, 99.99%) wrapped around a resistively heated tungsten filament. The Zn flux from the source was monitored using a quartz crystal microbalance (QCM) and the total amount of Zn deposited was further quantified by measuring the area of the high-temperature Zn desorption feature in the TPD spectra. Since in each TPD run with a Zn-modified surface the sample was heated to a sufficiently high temperature (1200 K) to cause the Zn to desorb completely, freshly prepared Zn-modified surfaces were used in all of the TPD runs.

The structure of Zn-modified Pt(111) surfaces has previously been reported in detail.\[55\] In this previous study it was shown that Zn-deposition with the Pt(111) sample held at or below room temperature produces Zn adatoms. Annealing between 600 and 700 K causes the adatoms to diffuse into the surface, while heating to higher temperatures induces Zn desorption. For low Zn coverages, the equilibrium structure of the annealed surface is such that the Zn is present in the second and third layers. Thus, in order to provide a model alloy surface that contained both Zn and Pt sites, surfaces with Zn adatoms that were produced at low temperatures were used in this study. Note that in addition to providing Zn sites on the surface, Zn adatoms also influence the electronic properties and reactivity of nearby surface Pt atoms in manner similar to that observed for the bulk alloy.

3.3 Results

TPD data obtained following exposure of the clean and Zn-modified Pt(111) surfaces at 115 K to 0.6 L of furfural are displayed in Figure 3.1 through Figure 3.3. As shown by
the bottom curve in Figure 3.1, for Zn-free Pt(111) weakly adsorbed molecular furfural desorbed in two overlapping peaks centered at 185 and 195 K with an additional peak at 225 K due to a slightly more strongly bond species. Above 225 K, gaseous reaction products were detected for this surface with the primary ones being CO and H₂ as shown in Figure 3.2. CO desorbed in two overlapping peaks centered at 390 and 415 K, while H₂ desorbed in a large peak at 430 K and a series of much less-intense peaks between 500 and 650 K. The CO peaks and the large H₂ peak are both consistent with desorption-limited products,[66] thus demonstrating that adsorbed furfural decomposes at lower temperatures. The only other product detected was a small amount of propene (m/e 41) which desorbed at 365 K indicating that both C-C and C-O bond cleavage in adsorbed furfural commences at or below this temperature. The TPD results for furfural on Pt(111) are similar to those reported previously for the reaction of acetaldehyde and glycolaldehyde on this surface.[39]

Figure 3.1:Furfural desorption spectra obtained during TPD of Zn-modified Pt(111) surface dosed with 0.6 L of furfural spectra as a function of the Zn coverage.
Figure 3.2: TPD spectra obtained following exposure of the Pt(111) surface to 0.6 L of furfural.
Figure 3.3: TPD spectra for (a) m/e=2 H$_2$, (b) m/e=18 H$_2$O, and (c) m/e=28 CO from Zn/Pt(111) as a function of Zn coverage. Each sample was dosed with 0.6 L furfural at 115 K.
TPD data for the reaction of furfural on Pt(111) modified with 0.1, 0.4 and 0.8 ML of Zn adatoms are displayed in Figure 3.3. In each experiment, the sample, held at 115 K, was dosed with 0.6 L of furfural. The furfural TPD data for Zn-free Pt(111) are also included in the figure for comparison. These data show that adding Zn to the Pt(111) surface causes significant changes in the stability and reaction pathways for adsorbed furfural. As shown in Figure 3.1, which displays the TPD curves for desorption of molecular furfural, the parent molecule still desorbed in two overlapping peaks between 185 and 195 K, but the higher-temperature furfural peak at 225 K decreased in intensity with increasing Zn coverage and was not observed for the 0.4 and 0.8 ML Zn/Pt(111) surfaces. The amount of molecular furfural desorbing from the Zn-modified surfaces was also significantly less than that from the Zn-free surface suggesting that the Zn adatoms decrease the furfural sticking probability. More dramatic changes were observed for the $\text{H}_2$ and CO products (Figure 3.3) which were produced at higher temperatures on the Zn-modified surfaces. Additionally, a small amount of $\text{H}_2\text{O}$ and $\text{CO}_2$ were also produced on the Zn-modified surfaces.

For 0.1 ML Zn/Pt(111), CO desorbed in two peaks centered at 400 K and 525 K (Figure 3.3(c)). Upon increasing the Zn coverage to 0.4 ML, the 400 K CO peak disappeared, indicating that it corresponds to CO adsorbed on Zn-free portions of the surface. The CO peak at 525 K persisted for Zn coverages up to 0.4 ML, but was absent from the 0.8 ML Zn surface. For 0.8 ML Zn/Pt(111), the CO peak at 525 K was absent and the only CO features were two small peaks centered at 750 K and 900 K.

As shown in Figure 3.3(a), for all of the furfural-dosed surfaces $\text{H}_2$ was produced in a series of overlapping peaks over a wide temperature range. The general trends in the $\text{H}_2$
desorption data with increasing Zn adatom coverage include a rapid decrease in the intensity of the H$_2$ peak at 450 K which dominated the spectrum for the Zn-free surface, and a shift of the remaining H$_2$ features to higher temperatures. For example, for 0.4 ML Zn/Pt(111), the H$_2$ desorption spectrum consists of a broad feature that spans between 500 K and 800 K. Small amounts of H$_2$O (Figure 3.3(b)) and a trace amount of CO$_2$ were also produced via reaction of furfural on the Zn-modified Pt(111) surfaces. For 0.1 ML Zn/Pt(111) a broad H$_2$O the peak is evident at 520 K (Figure 3.3(b)). This peak increases in intensity and shifts to higher temperatures with increasing Zn coverage. The CO$_2$ product (not shown in the figure) was only observed for the 0.4 and 0.8 ML Zn coverages and gave rise to a small peak between 500 and 675 K.
Figure 3.4: HREEL spectra as a function of temperature for Pt (111) surface dosed with 0.6L furfural at 115K.
HREEL spectra collected as a function of temperature for Zn-free and 0.4 ML Zn Pt(111) surfaces dosed with 0.6 L of furfural at 115 K are displayed in Figure 3.4 and Figure 3.5, respectively. The spectra corresponding to surface temperatures higher than the dosing temperature were obtained by briefly heating the dosed sample to the indicated temperature and then rapidly quenching to 115 K at which point the spectrum was collected. For the Zn-free Pt(111) surface, the HREEL spectrum obtained after dosing at 115 K (Figure 3.4) is consistent with the IR and Raman spectra of furfural[67-69] and the HREEL spectrum of molecular furfural adsorbed on Mo2C/Mo(110) and Mo2C/Mo(100) at low temperature.[65, 70] Peak assignments for the spectrum of furfural on Pt(111) at 115 K were made by comparison to those reported for the aforementioned reference spectra and are reported in Table 3.1. Notable peaks in the spectrum include the v(C=O) stretch at 1665 cm\(^{-1}\) and the \(v_{\text{aldd}}(\text{CH})\) stretch at 2790 cm\(^{-1}\), both of which are indicative of the aldehyde functional group.
Table 3.1: Vibrational mod assignments of furfural

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu)_{(CH)}</td>
<td>3030-3160</td>
</tr>
<tr>
<td>(\nu)_{aldehyde(CH)}</td>
<td>2813-2858</td>
</tr>
<tr>
<td>(\nu)(C(=)O)</td>
<td>1665-1695</td>
</tr>
<tr>
<td>Ring Breath</td>
<td>-</td>
</tr>
<tr>
<td>(\nu)(C(=)C)</td>
<td>1393-1479</td>
</tr>
<tr>
<td>(\delta)(OCH)</td>
<td>-</td>
</tr>
<tr>
<td>(\rho)(CH), (\gamma)(CH)</td>
<td>755-885</td>
</tr>
<tr>
<td>(\rho)_{aldehyde(CH)}</td>
<td>-</td>
</tr>
<tr>
<td>(\rho)<em>{CH}, (\gamma)</em>{aldehyde(CH)}</td>
<td>-</td>
</tr>
<tr>
<td>(\nu)_{(CO)}</td>
<td>-</td>
</tr>
<tr>
<td>Ring Breath</td>
<td>-</td>
</tr>
<tr>
<td>(\gamma)(CH)</td>
<td>-</td>
</tr>
<tr>
<td>(\gamma)_{aldehyde(CH)}</td>
<td>-</td>
</tr>
<tr>
<td>Ring Breath</td>
<td>500-630</td>
</tr>
<tr>
<td>(\nu)(CH)_{(ring)}</td>
<td>-</td>
</tr>
<tr>
<td>(\nu)_{(OCC)}</td>
<td>-</td>
</tr>
<tr>
<td>(\nu)(CC)_{(ring, aldehyde)}</td>
<td>-</td>
</tr>
</tbody>
</table>

s – symmetric, as – asymmetric, b – bend, v – stretch, \(\delta\) – deformation, \(\rho\) – rock, \(\gamma\) – wag, \(\chi\) – scissor

Heating the furfural-dosed Pt(111) surface to 155 K produced only minor changes in the intensities of the peaks in the HREEL spectrum. Further heating to 205 K, however, resulted in significant changes, including decreases in the intensities of the aldehyde \(\nu\)(C\(=\)O) stretch at 1665 cm\(^{-1}\), the ring breathing modes at 1015 and 1565 cm\(^{-1}\), and the \(\nu\)(C\(=\)C) stretch at 1450 cm\(^{-1}\). Large peaks at 1805 cm\(^{-1}\) and 2050 cm\(^{-1}\), which are indicative of the \(\nu\)(C\(=\)O) mode of atop and bridging CO species on Pt(111),[71] also emerged indicating that cleavage of the C-CHO bond in the adsorbed furfural has commenced by this temperature.

Heating to 250 K and then 300 K caused growth in the intensities of the \(\nu\)(C\(=\)O) peaks of atop and bridging CO at 1805 cm\(^{-1}\) and 2050 cm\(^{-1}\), and the disappearance of the \(\nu\)_{ring}(CH) peak at 3125 cm\(^{-1}\) along with a concomitant increase in the intensities of several
overlapping $\nu$(CH) peaks between 2700 cm$^{-1}$ and 3000 cm$^{-1}$. The changes in the C-H stretching region indicate a loss of the aromatic character of the remaining hydrocarbon species on the surface. This is further corroborated by the disappearance of the $\gamma_{\text{ring}}$(OCC) (585 cm$^{-1}$) and $\gamma_{\text{ring}}$(CH) (780 cm$^{-1}$) peaks upon heating to 300 K. Additional heating resulted in decomposition of the remaining hydrocarbon fragments on the surface and the HREEL spectra contained only features indicative of atop and bridging CO.
Figure 3.5: HREEL spectra as a function of temperature for 0.4 ML Zn/Pt (111) surface dosed with 0.6L furfural at 115K.
HREEL spectra as a function of temperature for furfural-dosed, Zn-modified Pt(111) are displayed in Figure 3.5. For these studies a 0.4 ML Zn coverage was selected as a representative Zn adatom surface. The spectrum obtained after dosing 0.6 L of furfural at 115 K was nearly identical to that obtained from clean Pt(111) at the same temperature and was consistent the IR and Raman spectra of furfural.[65, 67-70] Peak assignments are listed in Table 3.1. Notable features in the spectrum include the $\gamma_s$(CH) and $\gamma_{as}$(CH) peak at 780 cm$^{-1}$, the $\nu$(C=O) stretch at 1670 cm$^{-1}$, and the $\nu_{ald}$(CH) stretch at 2790 cm$^{-1}$.

Heating to 200 K, which as shown in Figure 3.1 is sufficient to desorb any weakly adsorbed furfural, resulted in considerable alteration of the relative intensities of the peaks. The most noticeable being a dramatic decrease in the relative intensity of the $\nu$(C=O) stretch which also shifted slightly from 1670 cm$^{-1}$ to 1655 cm$^{-1}$, and an increase in the intensity of the in-plane ring stretching modes between 900 and 1250 cm$^{-1}$. A slight shift in position of the $\nu_{ald}$(CH) mode of the aldehyde group from 2790 cm$^{-1}$ to 2890 cm$^{-1}$ also occurred upon heating to 200 K.

Heating from 200 K to 250 K caused the $\nu$(C=O) stretch of the aldehyde group at 1655 cm$^{-1}$ to further decrease in intensity. As will be discussed below, the disappearance of this peak may be due to a shift from an $\eta^1$(O) to an $\eta^2$(C, O) bonding configuration for the aldehyde carbonyl. Additional significant changes that occurred upon heating to 250 K include a downward shift in the position of the $\gamma_s$(CH) and $\gamma_{as}$(CH) wagging modes of the aromatic ring from 780 cm$^{-1}$ to 725 cm$^{-1}$ and a large decrease in the intensity of the $\nu_{ring}$(OCC) mode at 585 cm$^{-1}$. 
Except for a gradual decrease in the intensity of all of the peaks, heating from 250 K to 400 K produced relatively few changes in the spectrum, with the only significant one being a slight downward shift in the position of the ν(CH) stretch near 3120 cm$^{-1}$. This indicates that the adsorbed intermediates were relatively stable in this temperature range. It is notable that in contrast to clean Pt(111), these HREELS data show that the aromatic ring of adsorbed furfural remains largely intact on the Zn-modified surface at temperatures up to 475 K. Further increasing the temperature to 550 K resulted in the decomposition of the surface intermediate to CO and H$_2$, as evidenced by the emergence of a ν(C=O) stretch at 2050 cm$^{-1}$ indicative of atop CO and the near disappearance of the peaks associated with the furan ring.

3.4 Discussion

It is useful to first consider the adsorption and reaction of furfural on the Zn-free Pt(111) surface. The TPD data (Figure 3.2) shows that furfural undergoes unselective decomposition on this surface to produce primarily CO and H$_2$, and a trace amount of propene. Since the combined CO and propene products have a carbon to oxygen ratio much less than the 5:2 ratio in the furfural reactant, some carbon must have been deposited on the surface. The HREELS results in conjunction with data from the literature provide insight into the intermediates involved in this unselective decomposition pathway. Previous studies have shown that the most stable adsorption geometry for furan on Pt(111) is with the planar aromatic ring lying parallel to the surface.[72] Small aldehydes are also known to undergo C-H cleavage in the aldehyde group at temperatures below 200 K on
this surface to form acyl intermediates[39, 73] which are susceptible to decarbonylation upon heating. For furfural, both of these bonding modes need to be considered.

The HREEL spectrum of the furfural-dosed surface at and below 205 K is dominated by the peak at 780 cm\(^{-1}\) which is due to the out-of-plane C-H wagging modes of the furan ring. In contrast, the in-plane \(\nu_{\text{ring}}(\text{CO})\) and ring breathing modes between 1000 and 1200 cm\(^{-1}\) are of much lower intensity. These relative intensities differ from that in the IR spectrum of gaseous furfural where the in-plane and out-of-plane ring modes have similar cross-sections.[67] Sum frequency generation vibrational spectroscopy studies by Kliewer et al.[72] have shown that furan adsorbs on Pt(111) with the ring parallel to the surface. Assuming a similar bonding configuration for furfural on Pt(111), the dipole moments associated with the in-plane modes would be largely shielded by the induced image dipoles in the metal resulting in low adsorption cross-sections which is consistent with the HREELS data reported here.

The HREELS data in Figure 3.4 also do not provide any evidence for strong interaction of the aldehyde carbonyl in furfural with the Pt(111) surface. Note that below 250 K the spectrum of the furfural-dosed surface contains a \(\nu_{\text{ald}}(\text{C}=\text{O})\) peak at 1665cm\(^{-1}\) which is essentially at the same position as that in the IR spectrum of the free molecule.[67] This peak would be expected to be nearly absent (due to the surface dipole selection rules) and shift significantly to lower wavenumbers if the aldehyde group was in an \(\eta^2(\text{C,O})\) configuration in which both the C and O are bonded to the surface.[39, 65] Formation of an acyl intermediate via cleavage of the aldehyde C-H would also cause a shift to lower wavenumbers[39] Acyl formation at temperatures below 250 K can also be ruled out by
the presence of the C-H stretching peak at 2790 cm$^{-1}$ which is characteristic of the aldehyde C-H bond.

The HREEL data, therefore, show that furfural adsorbs on Pt(111) with the furan ring situated either parallel or nearly parallel to the surface, and that the aldehyde carbonyl does not interact strongly with the surface. Thus, the surface bonding appears to occur via the π-orbitals in the ring. This conclusion is consistent with a recent study by Liu et al.[74] in which DFT calculations indicated that the most stable adsorption geometry for furfural on Pt(111) was with the aromatic ring centered on a three-fold hollow site and the aldehyde group tilted away from the surface. They also concluded that the largest bonding contribution was due to interaction of the unsaturated C=C bonds in the ring with the surface. It is noteworthy that this result is somewhat different than what they[74] and others[75] have obtained by DFT for the adsorption of furfural on Pd(111) where both the aromatic ring and the aldehyde carbonyl are parallel to the surface in the most stable adsorption geometry.

The HREEL data in Figure 3.4 also show that C-C bond scission and ring opening in adsorbed furfural on Pt(111) commences by 205 K. This is evident by the appearance of ν(CO) peaks for bridging (1805 cm$^{-1}$) and atop (2050 cm$^{-1}$) CO and a new, distinct ν(C-H) peak at 2890 cm$^{-1}$ which is characteristic of aliphatic CHx groups on the surface. Ring opening is also demonstrated by the production of a small amount of propene at 365 K during TPD. Above 300 K decomposition of the furfural is nearly complete with adsorbed CO and small hydrocarbon fragments being the primary surface species.

The TPD results show that furfural is significantly more stable on the Zn-modified Pt(111) surfaces with reaction-limited decomposition products desorbing at temperatures
above 450 K. This stability is also reflected in the HREELS data obtained from the 0.4 ML Zn/Pt(111) surface. At 200 K, the HREEL spectrum is consistent with the IR spectrum of molecular furfural (see Table 3.1),[67] and in contrast to the corresponding data form Zn-free Pt(111), the relative intensities of the in-plane and out-of-plane ring modes suggest that the furan ring is not situated parallel to the surface. The large decrease in the relative intensity of the v(C=O) peak upon heating from 150 K to 250 K is consistent with the carbonyl of the aldehyde group being in an η²(C,O) configuration in which both the C and O are bonded to the surface,[22] and with what has been reported previously for both acetaldehyde and glycolaldehyde on Zn-modified Pt(111).[39] In these previous studies it was concluded based on XPS data that the O atom in the aldehyde carbonyl is bonded to a Zn site and the C is bonded to Pt. We, therefore, conclude that there is a similar bonding configuration for the aldehyde group in furfural on Zn-modified Pt(111) surfaces at low temperatures. This bonding configuration is shown schematically in Figure 3.6.

**Figure 3.6:** Proposed pathways and intermediates for the adsorption and reaction of furfural on Pt(111) and Zn/Pt(111) surfaces.
Changes in the structure and/or bonding of the adsorbed furfural is apparent upon heating from 200 to 250 K. The HREELS data show little alteration in the peaks associated with the aromatic ring between 800 and 1450 cm\(^{-1}\) as well as the furan ring C-H stretch at 3125 cm\(^{-1}\), thus indicating that the furan ring remains intact. There are, however, two significant changes in the spectrum, a shift of the lower energy \(\nu(CH)\) peak from 2790 to 2890 cm\(^{-1}\), and a shift of the intense peak at 780 cm\(^{-1}\) due to the ring \(\gamma_s(CH)\) and \(\gamma_{as}(CH)\) modes to 725 cm\(^{-1}\). The shift in the position of the \(\nu(CH)\) peak is significant because it indicates some alteration in the bonding or structure of the -CHO group. It is possible that this shift may be related to the formation of an \(\eta^2(C, O)\) intermediate. It is also noteworthy that this C-H stretch, which is distinct from that associated with the furan ring (3125 cm\(^{-1}\)), is apparent for temperatures up to 475 K, since this argues against cleavage of the C-H bond in the –CHO group and the formation of an acyl intermediate. Note that this conclusion is consistent with what has been reported previously for acetaldehyde and glycolaldehyde where the addition of Zn to the Pt(111) was also found to hinder acyl formation which is facile on the Zn-free surface.[39]

The shift in the \(\gamma_s(CH) + \gamma_{as}(CH)\) peak to lower wavenumbers is more difficult to explain. The HREELS data do not provide any evidence for a strong interaction of the furan ring with the surface, since these are the only ring-related modes that are altered. In our previous studies of the reaction of acetaldehyde and glyceraldehyde on Zn-modified Pt(111) it was concluded based on HREELS data that the \(\eta^2(C,O)\) bonded carbonyl group in these molecules undergo C-O bond cleavage near room temperature. A similar reaction would therefore be expected for the \(\eta^2(C, O)\) bonded furfural on this surface. By this scenario both the shifts in the \(\nu_{ald}(CH)\) and \(\gamma_{ring}(CH)\) modes could result from this C-O bond
cleavage reaction. The IR spectra of substituted furans provide some support for this. Note that in the IR spectra of furfural, 2-furfuryl-alcohol and 2-methyl-furan the $\gamma_{\text{ring}}$(CH) mode is located at 754, 735, and 722 cm$^{-1}$ [67, 76], respectively, indicating that removal of the electron withdrawing oxygen in the substituent group causes the $\gamma_{\text{ring}}$(CH) modes to shift to lower wavenumbers. The production of a small amount of water between 400 and 600 K during TPD of furfural-dosed Zn-modified Pt(111) surfaces (see Figure 3.3(b)) also provides some support for C-O cleavage in the adsorbed intermediate.

Based on the TPD data and the analysis of the HREEL spectra we propose the reaction pathways and intermediates shown schematically in Figure 3.6 for the reaction of furfural on Zn-modified Pt(111) surfaces. At low temperatures (< 250 K), furfural interacts with the surface primarily via the aldehyde carbonyl with the aromatic furan ring tilted away from the surface. At 200 K this carbonyl bonds to the surface in an $\eta^2$(C, O) configuration. By analogy to results reported in previous studies for acetaldehyde and glycolaldehyde on Zn-modified Pt(111),[39] it is assumed that the oxygen in the carbonyl is bonded to a Zn site and the carbon is bonded to a Pt site. The bonding to the surface for this intermediate occurs via electron donation from the metal d-orbitals into the unoccupied $\pi^*$ anti-bonding orbitals of the carbonyl. This causes a reduction in the strength of the C-O bond which helps facilitate its cleavage which occurs between 250 K and 300 K. As shown in Figure 3.6, this produces a (C$_4$H$_3$O)-CH= intermediate. This intermediate is relatively stable since it remains intact up to 400 K (as determined by HREELS). Recall that on the pristine Pt surface furfural decomposed completely and unselectively below 300 K. The thermal stability of the (C$_4$H$_3$O)-CH= intermediate on the Zn-modified surface therefore further
demonstrates that the addition of Zn to Pt decreases the metal’s activity for C-C and C-H bond cleavage.

Under typical HDO reaction conditions where there would be a high converge of H atoms on the catalyst, one would anticipate that the (C₄H₅O)-CH= intermediate could be hydrogenated to produce 2-methyl-furan. Thus, the results of this study suggest that PtZn may exhibit high selectivity for the HDO of furfural to produce 2-methyl-furan. The results of this study also provide insight into why addition of an oxyphilic metal, such as Zn, to group 10 metals enhances activity for selective HDO of aromatic oxygenates without hydrogenation of the aromatic ring. The key observation obtained here is that the Zn significantly weakens the interaction of the furan ring with the Pt surface producing intermediates in which the ring is tilted away from the surface thereby preventing its hydrogenation.

3.5 Conclusions

This study provides insight into the adsorption and reaction of the biomass-derived oxygenate, furfural, on Pt(111) and Zn-modified Pt(111) surfaces. For Zn-free Pt(111), furfural primarily interacts with the surface via the aromatic ring and undergoes C-C bond scission and ring opening at temperatures as low as 200 K which leads to unselective decomposition to CO and H₂ at higher temperatures. Modifying the Pt(111) surface with Zn adatoms significantly alters the bonding of furfural with an η²(C, O) configuration in which the furan ring is tilted away from the surface being the most stable at 200 K. This bonding configuration results in a weakening of the carbonyl C-O bond facilitating its cleavage. The lack of a strong interaction of the aromatic furan ring with the Zn-modified
surface would also be expected to help limit hydrogenation of the ring under typical HDO reaction conditions. These results suggest that PtZn catalysts may have high activity for the selective HDO of furfural to produce methyfuran.
Chapter 4 Lignin-Derived Oxygenate Reforming on a Bimetallic Surface: the Reaction of Benzaldehyde On Zn/Pt(111)²

Summary

Temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) were used to characterize the adsorption and reaction of benzaldehyde (C₆H₅CHO) on hydrogen-covered Pt(111) and Zn-modified Pt(111) surfaces. Benzaldehyde was found to interact with Pt(111) via both the phenyl ring and carbonyl of the aldehyde group. This bonding configuration facilitates unselective decomposition of the benzaldehyde to produce CO, H₂, and small hydrocarbon fragments at relatively low temperatures. On the other hand, benzaldehyde was found to bond to Zn-decorated Pt(111) surface exclusively via the carbonyl group in an η²(C, O) configuration, with the phenyl ring tilted away from the surface. This configuration weakens C-O bond in the carbonyl facilitating its cleavage and helps prevent hydrogenation of the phenyl ring.

² This chapter was published as Shi, Daming, and John M. Vohs. Surface Science 650 (2016): 161-166.
4.1 Introduction

There is an increasing interest in the development of technologies for converting lignocellulosic biomass into chemicals and fuels to reduce our dependence on non-sustainable traditional fossil fuels such as petroleum and natural gas [16, 59, 60]. Of the three components of biomass, cellulose, hemicellulose, and lignin, the conversion of the two former into more useful products has received the most attention from the research community [13, 16, 17, 77]; however, lignin, which constitutes 15-30% by weight and up to 40% by energy content of biomass [78], is a valuable resource. Lignin is an amorphous polymer of oxygenated aromatic subunits (e.g. coniferyl and sinapyl alcohols) that gives plants their structural integrity. The aromatic nature of lignin makes it an attractive feedstock for the production of high value aromatic compounds [11, 79].

Depolymerization of lignin via fast pyrolysis or other means produces a range of oxygenated aromatics with phenol, anisole, benzaldehyde, salicylaldehyde, and guaiacol being typical examples [11, 40-43]. The high oxygen content in many of these molecules is problematic since it reduces their fuel value and suitability as feedstock for fine chemicals. Thus, upgrading by partial or complete oxygen removal is likely to be necessary for any commercial process using lignin as a starting material. This has motivated studies of the catalytic hydrodeoxygenation (HDO) of lignin-derived molecules [3, 11]. Several studies of the use of supported group 10 metal catalysts (Ni, Pt and Pd) for this purpose have recently appeared in the literature [24, 44-47]. These monometallic catalysts, however, are not highly selective for HDO and tend to also promote the undesired hydrogenation of the phenyl rings.
Bimetallic catalyst composed of a group 10 metal alloyed with a more oxyphilic metal, such as Fe, Sn, or Zn, have proven to be more selective for oxygen removal without ring hydrogenation [3, 24-26, 43, 48-52]. Our previous studies of model PtZn catalysts have shown that at least for molecules containing aldehyde functional groups, the more oxyphilic Zn provides a binding site for the oxygen of the carbonyl group with the carbon being bound to Pt [39, 80, 81]. This bonding configuration results in a weakening of the C-O bond thereby facilitating its scission. The mechanism by which alloying with an oxyphilic metal decreases activity for hydrogenation of phenyl rings is less clear. It has been suggested, however, that it may decrease ring-surface interactions and alter the adsorption configuration [82-85]. The goal of the work reported here was to test this hypothesis and determine how alloying Pt with Zn affects the interaction of the phenyl rings in oxygenated aromatic compounds with the catalyst surface and the suitability of such catalysts for selective HDO of lignin-derived aromatic compounds. We have used a surface science approach in this work and studied the adsorption and reaction of benzaldehyde (C6H5CHO) on a Zn-decorated Pt(111) surface using temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS).

4.2 Experimental

HREELS and TPD experiments were conducted in an ultrahigh vacuum (UHV) apparatus with a background pressure of 2×10^{-10} torr. The system was equipped with a quadruple mass spectrometer (SRS RGA200), an ion sputter gun (PHI electronics) and an HREEL spectrometer (LK Technologies). The Pt(111) single crystal substrate was 10 mm
in diameter and oriented to within ±0.5°. The surface was cleaned by repeated cycles of 2 kV Ar⁺ ion bombardment at 600 K for 40 min, annealing at 1200 K in 2×10⁻⁸ torr O₂ for 15 min, and annealing at 1200 K in vacuum for 5 min. The Pt(111) crystal was spot-welded to two tantalum wires that were connected to UHV sample manipulator. The sample could be heated resistively and cooled to 110 K by conduction from a liquid N₂ reservoir.

Zn-decorated Pt(111) surfaces were prepared by exposing the Pt surface to a beam of Zn atoms produced using a thermal evaporative source that consisted of a small coil of Zn wire (Alfa Aesa, 99.99%) wrapped around a resistively heated tungsten filament. The Zn flux from the source was monitored using a quartz crystal microbalance (QCM) and the total amount of Zn deposited was further quantified by measuring the area of the high-temperature Zn desorption feature in the TPD spectra. We have previously characterized the structure of Zn-modified Pt(111) surfaces in detail [57]. For the Zn deposition conditions used here, the deposited Zn atoms remain on the surface and do not form an ordered overlayer.

The reactant, benzaldehyde (Sigma Aldrich, 99.5%) was contained in a glass vial attached to a stainless steel manifold that was connected to the main UHV apparatus via a variable leak valve. Hydrogen was contained in a lecture bottle that was attached to the same dosing line. Since we were interested in HDO activity and the propensity of the model catalysts to hydrogenate the phenyl ring in benzaldehyde, experiments were conducted using surfaces saturated with H₂ which were obtained by exposing the surface to 10 L of H₂. A 0.6 L exposure of benzaldehyde was used in both the TPD and HREEL experiments. This exposure was chosen based on a series of TPD experiments on Pt(111) which showed that it was sufficient to saturate the surface with benzaldehyde at low temperatures.
HREEL spectra were collected using a 4 eV electron beam, oriented at 60° with respect to the surface normal. The intensity of the elastic peak varied between 10k and 100k cps and had a full width half-maximum of ~40 cm⁻¹. All TPD data were collected using a 3K/s heating rate.

4.3 Results

4.1.1 Temperature Programmed Desorption (TPD)

TPD studies were performed for both Pt(111) and Zn-decorated Pt(111) surfaces that were pre-dosed with H₂ and then dosed with 0.6 L of benzaldehyde at a sample temperature of 115 K. As noted above, this benzaldehyde dosage was selected because it was sufficient to saturate each surface with the reactant as evidenced by a molecular benzaldehyde desorption peak at 200 K. Figure 4.1 displays TPD data obtained from the Zn-free Pt(111) surface. In addition to the molecular benzaldehyde peak at 200 K, other desorption products including, H₂, CO, CH₄, were observed at temperatures above 300 K. CO was produced in a broad feature between 360 and 480 K which was composed of at least two overlapping peaks. This temperature range is consistent with desorption-limited CO from Pt(111) [86] and thus demonstrates that C-C bond scission in the adsorbed benzaldehyde commences at or below 360 K. Meanwhile, H₂ was produced in a large peak at 350 K which can be assigned to recombinative desorption of H atoms [86], and a series of smaller reaction-limited peaks between 440 and 700 K. A small amount of methane (m/e 16) was also observed at 420 K, again indicating that C-C bond cleavage in the benzaldehyde occurs below this temperature. These TPD results for benzaldehyde on Pt(111) are similar to those reported previously for other aldehydes, such as acetaldehyde and furfural [39, 73, 80],
which also showed that the high activity of this surface for C-C bond scission results in decomposition of these molecules at relatively low temperatures.

Consistent with our previous studies [39, 80], decoration of the Pt(111) surface with Zn atoms caused significant changes in reactivity toward benzaldehyde with the most notable being a shift of the major products, CO and H\textsubscript{2}, to higher temperatures, and the emergence of toluene (C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}) and H\textsubscript{2}O as reaction products. These trends are apparent in Figure 4.2 which displays TPD curves for H\textsubscript{2}, CO, C\textsubscript{6}H\textsubscript{5}CH\textsubscript{3}, and H\textsubscript{2}O as a function of Zn coverage for H\textsubscript{2}-saturated Pt(111) dosed with 0.6 L of benzaldehyde. Desorption of molecular benzaldehyde at 200 K was also observed, but is not included in the figure.

Figure 4.1: TPD spectra obtained following exposure of the H\textsubscript{2}-saturated Pt(111) surface to 0.6 L of benzaldehyde.
As shown in Figure 4.2 (b), the CO peaks shifted to higher temperatures with increasing Zn coverage. For 0.1 ML Zn the CO peaks are centered at 450 and 520 K, and merge into a single peak centered at 520 K upon increasing the Zn coverage to 0.4 ML. For this coverage range the total amount of CO produced also decreased somewhat with increasing Zn coverage. At higher Zn coverages the CO peak at 520 K continued to decrease in intensity and was not observed for Zn coverages \( \geq 0.8 \) ML. These trends all
point to the Zn-modified surfaces having a lower activity for C-C bond scission in the adsorbed benzaldehyde.

The H$_2$ desorption curves in Figure 4.2 (a) also show an increase in peak temperature with increasing Zn coverage. Upon addition of 0.1 ML of Zn, the primary H$_2$ desorption peak, which appears at 350 K on the Zn-free surface, shifted to 435 K. A very broad H$_2$ desorption feature between 560 and 830 K also emerged. Both of these features increased somewhat in temperature with increasing Zn coverage. The possible origins of the H$_2$ peaks will be discussed in detail below, but the shift to higher temperature suggests that they are reaction limited rather than desorption limited as was observed for Zn-free Pt(111).

As noted above, addition of Zn adatoms to the Pt(111) surface also resulted in the emergence of peaks for H$_2$O and toluene in the TPD spectra of the benzaldehyde-dosed surface. As shown in Figure 4.2 (c) a broad water peak centered at 490 K is apparent for the 0.1 Zn/Pt(111) surface and both increases in intensity and temperature with increasing Zn coverage. Note that water was not produced on the Zn-free surface and its production on the Zn-modified surfaces demonstrates that these surfaces are active for C-O bond scission in the adsorbed benzaldehyde. The production of toluene on the Zn-modified surfaces as shown in Figure 4.2 (d) is particularly interesting since this is the desired product for the HDO of the benzaldehyde reactant. (This product was identified using spectra for m/e 91, 77, and 51). For the 0.1 ML Zn/Pt(111) surface toluene is produced at 430 K. This peak grew in intensity when the Zn coverage was increased to 0.4 ML, but was absent for high Zn coverages as shown in the figure for 0.8 ML of Zn.
4.1.2 High Resolution Electron Energy Loss Spectroscopy (HREELS)

HREEL spectra were collected as a function of temperature for Zn-free and Zn-decorated Pt(111) surfaces pre-dosed with H₂ and then dosed with 0.6 L benzaldehyde with the sample at 115 K. The spectra for the Zn-free and Zn-decorated surfaces are displayed in Figure 4.3 and Figure 4.4, respectively. Note that the spectra corresponding to higher temperatures were obtained by briefly heating the sample to the indicated temperature and then letting it cool back to 115 K at which point the spectrum was collected. For the Zn-free Pt(111) surface the spectrum obtained after dosing at 115 K contains peaks that are characteristic of molecular benzaldehyde and can be assigned via comparison to the corresponding IR and Raman spectra [87, 88]. Assignments of the primary peaks along with a comparison to those in the IR and Raman spectrum of benzaldehyde are given in Table 4.1. Notable peaks in the spectrum include the $\nu$(C=O) stretch at 1650 cm⁻¹, the $\nu_{\text{val}}$(C-H) stretch at 2750 cm⁻¹, and the $\nu_{\text{ring}}$(C-H) stretch at 3000 cm⁻¹.
Figure 4.3: HREEL spectra as a function of temperature for H₂-saturated Pt(111) dosed with 0.6 L benzaldehyde at 115K.
Table 4.1: vibrational mode assignment for benzaldehyde

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency cm$^{-1}$</th>
<th>( \text{IR/Raman} )</th>
<th>( \text{Pt (111)} )</th>
<th>( \text{Zn/Pt(111)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_{\text{ring}}(\text{CH}) )</td>
<td>3031-3104</td>
<td>3000</td>
<td>3000</td>
<td></td>
</tr>
<tr>
<td>( v_{\text{aldehyde}}(\text{CH}) )</td>
<td>2813</td>
<td>2750</td>
<td>2750</td>
<td></td>
</tr>
<tr>
<td>( v_{\text{aldehyde}}(\text{C=O}) )</td>
<td>1709</td>
<td>1650</td>
<td>1650</td>
<td></td>
</tr>
<tr>
<td>( v_{\text{aldehyde}}(\text{C-C}) + v_{\text{ring}}(\text{C-H})(\text{in-plane mode}) )</td>
<td>1203,827</td>
<td>1160,820</td>
<td>1155,815</td>
<td></td>
</tr>
<tr>
<td>( \gamma (\text{C-C}) ) (out of plane mode)</td>
<td>1005</td>
<td>980</td>
<td>980</td>
<td></td>
</tr>
<tr>
<td>( \gamma (\text{CH}) ) (out of plane mode)</td>
<td>742</td>
<td>750</td>
<td>735</td>
<td></td>
</tr>
<tr>
<td>( \gamma (\text{CH}) ) (out of plane mode)</td>
<td>688</td>
<td>670</td>
<td>680</td>
<td></td>
</tr>
</tbody>
</table>

s – symmetric, as – asymmetric, b – bend, \( v \) – stretch, \( \delta \) – deformation, \( \rho \) – rock, \( \gamma \) – wag, \( \chi \) – scissor

Only minor changes in the spectrum were observed upon heating to 180 K, but more significant changes occurred upon heating to 210 K, a temperature sufficient to desorb weakly bound molecular benzaldehyde as demonstrated by the TPD results. These changes include a diminution in the intensity of the \( v(\text{C=O}) \) stretch at 1650 cm$^{-1}$ along with the appearance of a new peak at 1615 cm$^{-1}$, and decreases in the intensities of the \( v_{\text{ring}}(\text{C-H}) \) mode at 3000 cm$^{-1}$ and the in-plane \( v(\text{C-C}) \) modes at 820 and 1160 cm$^{-1}$ relative to the out-of-plane ring modes between 650 and 800 cm$^{-1}$. As will be discussed below, these changes can be attributed to a change in the bonding configuration of the chemisorbed benzaldehyde molecule.

Heating the sample to 250 and then 300 K caused several important changes in the spectrum. In the 500-1000 cm$^{-1}$ region the peak at 820 cm$^{-1}$ became dominate and the previously intense peaks at 670 and 750 cm$^{-1}$ disappeared, while in the \( v(\text{C-H}) \) region a new peak emerged at 2880 cm$^{-1}$ along with the disappearance of the \( v_{\text{ring}}(\text{C-H}) \) stretch at 3000 cm$^{-1}$. This latter change signifies the loss of aromaticity in the adsorbed intermediate which is due to either ring hydrogenation or C-C bond cleavage and ring opening. Finally,
peaks grow in at 1650, 1775 and 2030 cm\(^{-1}\). As will be discussed below, these peaks can be assigned to the \(v(C=O)\) modes of CO adsorbed on threefold, bridge, and atop sites, respectively, and indicate the onset of scission of the C-CO bond in the adsorbed intermediate.

Further heating to 400 K led to the growth of the \(v(C=O)\) peaks at 1650, 1775 and 2030 cm\(^{-1}\). A new peak also grows in at 750 cm\(^{-1}\). Above 400 K the intensities of all the peaks decrease and a new peak appears at 450 cm\(^{-1}\) that can be assigned to a Pt-C stretch. Together with the TPD data, these results show that C-C and C-H bond scission in the adsorbed benzaldehyde commences by 400 K resulting in unselective decomposition to produce adsorbed CO and small hydrocarbon fragments.

HREEL spectra as a function of temperature for a benzaldehyde-dosed Zn-modified Pt(111) surface are displayed in Figure 4.4. A 0.4 ML Zn coverage was used here as a representative Zn adatom surface. The spectra were again obtained after saturating the surface with H\(_2\) and then dosing with 0.6 L benzaldehyde. As expected, at temperatures below 180 K the spectrum is nearly identical to that obtained in this temperature range for Zn-free Pt(111) and is consistent with the IR and Raman spectrum of benzaldehyde (see Table 4.1).
Figure 4.4: HREEL spectra as a function of temperature for H-saturated 0.4 ML Zn/Pt (111) surface dosed with 0.6 L benzaldehyde at 115K.
Heating to 210 K, which is sufficient to desorb physisorbed benzaldehyde, caused changes in both the relative intensities of the peaks and some peak positions. Notable changes include a decrease in the intensity of the ν(C=O) stretch at 1650 cm\(^{-1}\) and an increase in the intensity of the peak 980 cm\(^{-1}\) which is associated with the ν(C=C) stretch of the phenyl ring, and decreases in the relative intensities of γ(CH) (out of plane) peaks at 680 and 735 cm\(^{-1}\). A shift in the position of the ν\(_{\text{ald.}}\)(CH) peak from 2750 to 2820 cm\(^{-1}\) was also observed.

Heating to 250 K induced few changes in the spectrum, but heating to 300 K caused a further decrease in the intensity of the ν(C=O) stretch at 1650 cm\(^{-1}\). It is noteworthy that at this temperature, except for small alterations in the relative intensities, the majority of the peaks associated with the phenyl ring remain unchanged, and that the ν\(_{\text{ald.}}\)(C-H) stretch is still evident at 2820 cm\(^{-1}\) demonstrating that the CHO group remains intact. As will be discussed below, we attribute the large decrease in the intensity of the ν(C=O) stretch to the majority of the benzaldehyde molecules being bonded to the surface via the aldehyde group in an η\(^2\)(C, O) configuration as has been reported for other aldehydes, such as furfural, on Zn-modified Pt(111) [39, 80, 81].

Further heating of the benzaldehyde-dosed Zn/Pt(111) sample to 350 and then 400 K again resulted in relatively few changes in the spectrum except for the emergence of a ν(C=O) peak at 2000 cm\(^{-1}\) and a small ν(O-H) stretch at 3430 cm\(^{-1}\). The former can be assigned to atop CO which may be at least partially due to CO adsorption from the chamber background. The possible origin of the ν(O-H) stretch will be discussed below. Note that the ν\(_{\text{ring}}\)(C-H) peak at 3000 cm\(^{-1}\) remains unchanged indicating that the phenyl ring remains
intact at this temperature. Together these observations show that, in contrast to the Zn-free surface, the adsorbed benzaldehyde species is relatively stable on the Zn-modified surface. Further increasing the temperature from 400 K to 450 K and above resulted in decomposition of the surface intermediate to CO and H₂ as evidenced by a significant increase in the intensity of the \( \nu(C=O) \) peak at 2000 cm\(^{-1}\) due to atop CO.

4.2 Discussion

Let us first examine the adsorption and reaction of benzaldehyde on the Zn-free, H-covered Pt(111) surface. At temperatures below 250 K the HREELS data indicate that benzaldehyde adsorbs molecularly. The intensities of the in-plane \( \nu_{\text{ring}}(C-H) \) peak at 3000 cm\(^{-1}\) and the \( \nu(C-C) \) peaks at 820 and 1160 cm\(^{-1}\), relative to the out-of-plane \( \delta(CH) \) peaks between 650 and 800 cm\(^{-1}\) for chemisorbed benzaldehyde at 210 K are consistent with the phenyl ring being oriented parallel to the surface. (Note that vibrational modes oriented parallel to the surface induce an image dipole in the metal that significantly screens the dipole moment of the vibration resulting in a decrease in the excitation cross-section.) This conclusion is also consistent with a recent DFT study by Rasmussen and Hammer that showed that the adsorption of benzaldehyde on Pt(111) is dominated by interaction of the phenyl ring with the surface [89]. That study also showed that there are similar adsorption energies for configurations in which the C=O of the aldehyde group is either parallel or tilted away from the surface (both with the ring laying flat). The parallel geometry, which is essentially an \( \eta^2(C, O) \) bonding configuration for the aldehyde group, however, was found to result in a slight weakening of the C-O bond. In the HREEL data in the present
study it was observed that the $\nu_{\text{ald}}(C=O)$ stretch shifted from 1650 cm$^{-1}$ to 1615 cm$^{-1}$ providing evidence for this weakening. These observations along with a decrease in intensity of the $\nu_{\text{ald}}(C=O)$ mode upon desorption of the physisorbed benzaldehyde point to the carbonyl group being oriented parallel to the surface, as shown in Figure 4.5. This bonding configuration is also consistent with that reported previously for benzaldehyde on Pd(111) [90]

**Benzaldehyde on Pt(111) surface**

![Benzaldehyde on Pt(111) surface diagram](image)

**Benzaldehyde on 0.4 ML Zn/Pt(111) adatom surface**

![Benzaldehyde on 0.4 ML Zn/Pt(111) adatom surface diagram](image)

Figure 4.5: Proposed pathways and intermediates for the adsorption and reaction of benzaldehyde on Pt(111) and Zn/Pt(111) surfaces

Heating the benzaldehyde-dosed Pt(111) surface to 250 K resulted in loss of the aromatic character of the ring as signified by the shift of the primary $\nu$(CH) peak from 3000 cm$^{-1}$ to 2880 cm$^{-1}$ and the disappearance of the ring out-of-plane $\gamma$(CH) modes at 670 and 750 cm$^{-1}$. The $\nu_{\text{ald}}(C-H)$ stretch also disappeared, indicating that some C-H bond scission has occurred by this temperature. At higher temperatures significant decomposition of the adsorbed intermediate occurred as evidenced by the emergence of
peaks at 1650, 1775, and 2030 cm$^{-1}$ due to CO adsorbed in threefold, bridge, and atop sites respectively. Note that while the peak at 1650 cm$^{-1}$ is unusually low for threefold CO on Pt(111) [91, 92], it has been shown previously that co-adsorption of electron-donating molecules, such as benzene, can cause a significant decrease in the CO stretching frequencies by increasing the amount of back donation of $d$-electrons from the metal into the $\pi^*$ anti-bonding orbitals of the adsorbed CO [90, 93].

The appearance of an intense peak at 750 cm$^{-1}$ provides additional evidence for the decomposition of the adsorbed benzaldehyde. While it is difficult to definitively assign this peak, the two peak structure at 750 and 820 cm$^{-1}$ is similar to that observed for acetylene adsorbed on Pt(111) [94]. C-C bond scission in the phenyl ring of the adsorbed benzaldehyde could produce such acetylenic species.

Both the TPD and HREELS results demonstrate that benzaldehyde is more stable on the Zn-decorated Pt(111) compared clean Pt(111) with the adsorbed molecule staying largely intact up to 400 K. This is consistent with previous studies of the reaction of aldehydes and alcohols on Zn-modified Pt surfaces that show that Zn addition decreases the activity for both C-C and C-H bond scission [39, 80, 81, 95].

The bonding geometry for benzaldehyde on the Zn-modified surface is also different than that on the Zn-free surface. While some changes in the relative intensities of the in-plane and out-of-plane vibrational modes were observed upon heating from 180 to 210 K, significant diminution of the in-plane modes was not observed indicating that the phenyl ring is tilted away for the Zn-modified surface. In contrast, the decrease in the intensity of the $\nu_{\text{ald}}$(C=O) that occurs in the same temperature range indicates that the carbonyl group
is oriented nearly parallel to the surface. Together these results lead to the conclusion that benzaldehyde bonds to the Zn-modified surface via the carbonyl group in an $\eta^2$(C, O) configuration with the phenyl ring tilted away from the surface. This $\eta^2$(C, O) bonding configuration for the aldehyde group has also been observed in previous studies of the adsorption of other aldehydes (e.g. acetaldehyde, glycolaldehyde and furfural) on Zn-modified Pt(111) [39, 80]. Furthermore, in these previous studies it has been shown using both HREELS and XPS data that in this bonding configuration the O in the carbonyl is bonded to a Zn site while the C is bonded to a Pt site. We therefore propose the bonding configuration shown in Figure 4.5 for benzaldehyde on Zn-modified Pt(111).

These previous studies have suggested that since the $\eta^2$(C, O) bonding results in a weakening of the C-O bond, this bonding configuration helps facilitate C-O bond cleavage. This also appears to be the case for benzaldehyde on Zn-modified Pt(111) where both the TPD and HREELS provide evidence for C-O bond cleavage in adsorbed benzaldehyde near 400 K. In particular, a small amount of toluene is produced during TPD at 430 K and a $v$(O-H) peak at 3430 cm$^{-1}$, which is characteristic of an adsorbed hydroxyl group, appears in the HREEL spectrum near this temperature. At higher temperatures the remaining adsorbed benzaldehyde decomposes to produce CO and adsorbed hydrocarbon fragments.

Consistent with previous studies, the results obtained here provide further demonstration that the addition of Zn to Pt decreases activity for C-C and C-H bond cleavage. Our results also show that Zn addition significantly decreases the strength of bonding interactions between an phenyl ring and the Pt(111) surface and that the Zn atoms provide binding sites for the oxygen atoms in oxygenated organic molecules.
The \( \eta^2(C, O) \) bonding configuration for benzoic acid on Zn-modified Pt(111) with the phenyl ring being tilted away from the surface has several implications for the use of PtZn catalysts for HDO of lignin-derived oxygenated aromatic molecules. For example, the fact that phenyl ring interacts weakly with the PtZn surface will likely help decrease activity for both ring hydrogenation and ring opening under HDO reaction conditions. The \( \eta^2(C, O) \) bonding configuration for the aldehyde group also weakens the C-O bond which helps facilitate its cleavage as demonstrated by the production of toluene during TPD. This suggests that PtZn catalysts may be active for selective HDO of aldehyde functionalities. We are currently doing flow reactor studies of the HDO of benzoic acid and other lignin-derived model compounds in order to test these hypotheses. The results of these studies will be reported in a future publication.

4.3 Conclusions

The results obtained in this study provide considerable insight into the adsorption and reaction of benzoic acid on both Pt(111) and Zn-modified Pt(111) surfaces. Benzoic acid interacts strongly with the Pt(111) surface via both the phenyl ring and aldehyde functional group, with both the ring and the carbonyl group being parallel to the surface. Benzoic acid adsorbed in this configuration undergoes C-H and C-C bond scission at temperatures as low as 350 K which leads to unselective decomposition to \( \text{H}_2 \) and CO at higher temperatures. In contrast, significantly different surface-adsorbate bonding and reaction pathways occurred for benzoic acid on Zn-decorated Pt(111). For this surface bonding was exclusively via the aldehyde group in an \( \eta^2(C, O) \) configuration with the oxygen of the carbonyl bonded to a Zn site and the phenyl ring tilted away from the surface.
This bonding configuration prevented ring hydrogenation and ring opening and facilitated carbonyl C-O bond cleavage as evidence by the production of toluene.
Chapter 5  The use of Bimetallics to Control the Selectivity for the Upgrading of Lignin-Derived Oxygenates: Reaction of Anisole on Pt and PtZn Catalysts

Summary

The adsorption and reaction of anisole on Pt and PtZn catalysts was investigated using both model single crystal and high surface area supported metal catalysts. Temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) studies of the interaction of anisole with Pt(111) demonstrated that there is a strong interaction between the phenyl ring of anisole and the surface, resulting in C-O and C-H bond scission at relatively low temperatures. In contrast, anisole was observed to bond to a Zn-modified Pt(111) surface primarily via the oxygen at Zn sites or possibly adjacent Pt sites, with the phenyl ring tilted away from the surface. Such bonding configuration facilitated selective C-O bond cleavage producing phenyl groups and methoxide groups with the latter being bonded to the Zn sites. These results suggested that PtZn may be an effective catalyst for hydrodeoxygenation (HDO) of lignin-derived aromatic oxygenates with low activity for ring hydrogenation. This hypothesis was then tested and verified by investigating the reaction of anisole and H₂ over high surface area carbon-supported Pt and PtZn catalysts.

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Introduction

Lignocellulosic biomass is emerging as an attractive, sustainable carbon feedstock for the production of fuels and chemicals [11, 14, 96]. While in recent years much effort has been focused on catalytic processing of the cellulosic fraction of biomass for this purpose [16, 59, 60], the lignin fraction is also a useful resource and provides a feedstock for the production of high-value aromatic compounds [11, 79]. The refractory nature of lignin, however, makes its conversion to useful products more challenging than that of cellulose. Depolymerization of lignin is generally achieved via fast pyrolysis which produces a complex liquid mixture containing a range of substituted aromatics [97]. This bio-oil is highly oxygenated and subsequent hydrodeoxygenation (HDO) is usually required.

Conventional metal-sulfide based hydrotreating catalysts (e.g. sulfided CoMo) have been suggested for use in the upgrading and deoxygenation of lignin-derived aromatic oxygenates; unfortunately, they tend to produce less desirable ring saturation products and also rapidly deactivate due to coking [44, 48, 98, 99]. Some success has been obtained using group 10 metal catalysts (i.e. Ni, Pd, Pt), but they also promote hydrogenation of the aromatic rings [19, 20]. Alloying a group 10 metal with a second more oxyphilic metal (e.g. Fe, Sn, Zn) [24-27], however, has emerged as a promising strategy for producing HDO catalysts that exhibit high selectivity for the production of aromatic hydrocarbons from lignin-derived oxygenates. Multiple studies have shown that alloying Pt or Pd with Sn or Fe weakens the interaction of the aromatic ring with the metal surface, and it has been proposed that this may affect the ring hydrogenation activity by altering the bonding configuration of aromatic oxygenates from one where the ring is lying flat on the surface to one where adsorption occurs primarily via the oxygen functionality [83-85].
Recently our group has undertaken a series of mechanistic studies of the adsorption and reaction of benzaldehyde and other small aldehydes on Pt-Zn model catalysts consisting of a Pt(111) surface decorated with Zn adatoms [39, 81, 100]. Our studies of benzaldehyde on these catalysts provide direct evidence that alloying does indeed alter the bonding configuration of the phenyl ring with the ring tilting away from the surface upon Zn addition. Furthermore, these previous studies show that aldehydes bond to the Zn/Pt(111) surface via the carbonyl in an η2-configuration in which the oxygen in the carbonyl is bonded to a Zn site and the carbon is bonded to an adjacent Pt site. This bonding configuration results in a weakening of the C=O bond which helps facilitate its cleavage.

In the work described here we have extended our previous studies of the reactivity of Zn-modified Pt surfaces to include the adsorption and reaction of anisole (CH₃OC₆H₅). This molecule was chosen as a model aromatic compound that contains a C-O-C linkage which is commonly found in lignin-derived oxygenates [101-103]. Temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) were used to characterize the pathways and intermediates involved in the reaction of anisole on both Pt(111) and Zn/Pt(111) surfaces. Based on the results for the model catalysts we have predicted trends in selectivity for the reaction of anisole on high surface area supported Pt and PtZn catalysts. These predictions were then tested by measuring product selectivity for the reaction of anisole over Pt/C and PtZn/C catalysts under typical HDO reaction conditions. The results from the model and high surface area catalysts together provide useful insight into the active sites in bimetallic HDO catalysts as well as how alloying can be used to limit activity for ring hydrogenation.
4.5 Experimental

The model catalyst studies in this work were conducted in an ultra-high vacuum (UHV) apparatus described in detail in previous publications [39, 64, 65]. The system had a background pressure operated at \(2 \times 10^{-10}\) torr and was equipped with a quadruple mass spectrometer (SRS RGA200), an ion sputter gun (PHI electronics) and an HREEL spectrometer (LK Technologies). A Pt(111) single crystal substrate which was 10 mm in diameter and oriented to within ±0.5° was spot-welded to two tantalum wires that were connected to the UHV sample manipulator. The Pt(111) surface was cleaned by repeated cycles of 2 kV \(\text{Ar}^+\) ion bombardment at 600 K for 40 min, annealing at 1200 K under \(2 \times 10^{-8}\) torr \(\text{O}_2\) for 15 min, and annealing at 1200 K in vacuum for 5 min. The sample was heated resistively and cooled to 110 K by conduction from a liquid \(\text{N}_2\) reservoir.

Zn deposition on Pt(111) was obtained by exposing the Pt surface to a beam of Zn atoms produced from an effusive source consisting of a coil of Zn wire (Alfa Aesa, 99.99%) around a resistively heated tungsten filament. A quartz crystal microbalance (QCM) was used to monitor the Zn flux from the source and the total amount of Zn deposited was further quantified by measuring the area of the high-temperature Zn desorption feature in the TPD spectra [39, 57]. Detailed characterization of the structure of Zn-modified Pt(111) surfaces has been reported previously [57]. In that study it was shown that for initial submonolayer amounts of Zn deposited with Pt(111) sample held at or below room temperature, the Zn diffuses into the surface upon annealing between 600 and 700 K with the equilibrium structure being one where the Zn atoms reside in the second and third layer below the surface. For this structure there are no Zn sites present on the Pt(111) surface. Since for this study we wanted to investigate how Zn affects reactivity via electronic
interactions and its potential role as an active site for HDO, we chose to investigate Pt(111) surfaces that were decorated with Zn adatoms that were formed by Zn deposition with the Pt(111) sample below room temperature. Our previous studies have shown that Zn adatoms influence the electronic property of nearby surface Pt atoms in a manner similar to that in the bulk alloy [39].

For the UHV studies the anisole reactant (Sigma Aldrich, 99.7%) was contained in a glass vial attached to a stainless steel manifold that was connected to the main UHV apparatus via a variable leak valve. A saturation exposure of anisole (0.6 L) was used in both the TPD and HREEL experiments. A heating rate of 3 K/s was used in the TPD experiments and the HREEL spectra were collected using a 4 eV electron beam oriented at 60° with respect to the surface normal. The full width at half-maximum of the elastic peak obtained from the clean surface was typically 40 cm⁻¹. HREEL spectra were collected as a function of sample temperature. For temperatures greater than the dosing temperature the sample was heated at 3 K/s to the indicated temperature and then rapidly quenched to low temperature at which point the spectrum was collected.

Micro flow reactor studies were also carried out to determine the reactivity of carbon supported Pt and PtZn catalysts for the HDO of anisole and to provide comparison data to the model catalyst studies. Pt/C catalysts with 10 wt% Pt were prepared by impregnation of carbon black (Vulcan XC-72R) with a water/ethanol (4:1) solution of tetraammineplatinum (II) nitrate (Pt(NH₃)₄(NO₃)₂, 99.99%, Alfa Aesar). The 10 wt% PtZn/C samples were prepared by co-impregnation with water/ethanol (4:1) solution of Pt(NH₃)₄(NO₃)₂ and Zn(NO₃)₂•6H₂O. Prior to reaction studies the catalysts were reduced in flowing 5% H₂/He to 673 K with a heating ramp of 2 K/min, then to 773 K with heating
ramp of 1 K/min at which point it was held for 2 h. PtZn catalysts were prepared with Pt:Zn molar ratios of 1:1 (PtZn/C) and 1:3 (PtZn₃/C). Both the PtZn/C and PtZn₃/C catalysts had a total metals loading of 10 wt%.

A high-pressure flow reactor that was similar to that described by Luo et al. [58] was used in the reactor studies. The reactor consisted of a 20 cm long, stainless-steel tube (4.6-mm ID) that was heated in a tube furnace. A 1 wt% liquid solution of anisole (Sigma Aldrich, 99.7%) dissolved in n-heptane (Sigma Aldrich, 99%) was introduced into the reactor by an HPLC pump (Series III, Lab Alliance). The pump was also used to monitor the total pressure which was controlled by a back pressure regulator (KPB series, Swagelok) that was located downstream from the reactor. The pressure was fixed at 27.5 bar for all the experiments performed in this study. Hydrogen (Airgas, UHP grade) contained in a regulated, high-pressure cylinder was delivered to the reactor through 2.44 m of capillary tubing (50.8µm ID, Valco Instrument, Inc.). The H₂ flow rate was a function of the cylinder outlet pressure and the pressure drop across the capillary tube. For a typical experiment, the liquid flow rate was set as 0.1 ml/min, while the H₂ flow rate was kept constant at 5 ml/min (STP).

For each catalyst test, 0.05g of the catalyst was packed into the middle portion of the reactor and held in place by glass wool. Prior to rate measurements, each catalyst was pretreated by heating in 27.5 bar of flowing H₂ at 573 K for 30 min. Fresh samples were used for each experiment at a specified reaction condition. The liquid phase reaction products were collected at room temperature and a GC–MS (QP-5000, Shimadzu) was used for identification and quantification of the produces. Product selectivity was quantified using solutions with known concentrations as standards. The reactivity data
presented here were obtained 60 min after starting the reaction in order to allow steady state to be obtained.

4.6 Results and Discussion

5.3.1 Reaction of anisole on Pt(111)

The initial studies of the adsorption and reaction of anisole were performed for the Zn-free Pt(111) surface. TPD data collected as a function of coverage were used to determine the dosage required to saturate the surface with anisole, as determined by the appearance of a molecular anisole peak at 185 K corresponding to desorption of adsorbed multilayers. Based on these results, a 0.6 L anisole dose, which gives a coverage slightly more than one monolayer, was chosen for the more detailed TPD studies.

Figure 5.1: TPD spectra obtained following exposure of the Pt(111) surface to 0.6 L of anisole.
Figure 5.1 displays a complete set of TPD data obtained from the Zn-free Pt(111) surface for the 0.6 L anisole dose. The two low-temperature anisole desorption peaks at 185 and 215 K correspond to physisorbed multilayers and chemisorbed anisole, respectively. The only reaction products detected for this surface were H₂ and CO. Hydrogen was produced in two distinct peaks centered at 350 and 480 K, and a much broader feature that spanned from 530 K to 750 K. The H₂ peak at 350 K is at the same temperature as that reported for recombinative desorption of H atoms on Pt(111) [86] and therefore indicates that some C-H bond scission in adsorbed anisole has already occurred by this temperature. CO was primarily produced in two peaks centered at 420 and 480 K, with a smaller peak present at 530 K. From the TPD data alone it is not possible to definitively assign these peaks as desorption or reaction limited, although the fact that both CO and H₂ are produced at 480 K suggests that the CO at this temperature is reaction limited.
Figure 5.2: HREEL spectra as a function of temperature for Pt(111) dosed with 0.6 L anisole at 115 K.
HREELS was used to provide insight into the identity of adsorbed intermediates formed from anisole on the Pt(111) surface. HREEL spectra as function of temperature for Pt(111) dosed with 0.6 L of anisole at 115 K are displayed in Figure 5.2. As noted above, spectra corresponding to higher temperatures were obtained by briefly heating the sample to the indicated temperature and then letting it cool back to 115 K, at which point the spectrum was collected. As would be expected, the spectrum obtained at 115 K contains peaks that are characteristic of molecular anisole and can be assigned via comparison to the corresponding IR and Raman spectra [104-106]. Individual peak assignments are given in Figure 5.1

Table 5.1: Vibrational mode assignment of anisole on Pt and Zn/Pt(111) surface

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm⁻¹)</th>
<th>IR/Raman[104-106]</th>
<th>Pt (111)</th>
<th>Zn/Pt(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ(C-C)ring (out of plane mode)</td>
<td>509,513</td>
<td>500</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>Ring breathing</td>
<td>785</td>
<td>780</td>
<td>780</td>
<td></td>
</tr>
<tr>
<td>γ(C-H)ring (out of plane mode)</td>
<td>823,859</td>
<td>820</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>γ(C-H)ring (out of plane mode)</td>
<td>878,894</td>
<td>880</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>δ(C-H)ring (in plane mode)</td>
<td>1022,1029,997</td>
<td>1010</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>ν(O-Me) + b(C-H)ring (out of plane mode)</td>
<td>1182,1183</td>
<td>1150</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>ν(C-O) + ν(C-H)ring (in plane mode)</td>
<td>1247,1252,1253</td>
<td>1250</td>
<td>1250</td>
<td></td>
</tr>
<tr>
<td>δ(C-C)ring (in plane mode) + δ(C-H)methyl</td>
<td>1453,1436,1468,1422</td>
<td>1430</td>
<td>1440</td>
<td></td>
</tr>
<tr>
<td>ν(C-C)ring (in plane mode)</td>
<td>1588,1513</td>
<td>1550</td>
<td>1560</td>
<td></td>
</tr>
<tr>
<td>ν(C-H)methyl</td>
<td>2900</td>
<td>2870</td>
<td>2880</td>
<td></td>
</tr>
<tr>
<td>ν(C-H)ring</td>
<td>3004</td>
<td>3000</td>
<td>3000</td>
<td></td>
</tr>
<tr>
<td>ν(O-H)</td>
<td>-</td>
<td>-</td>
<td>3500</td>
<td></td>
</tr>
<tr>
<td>ν(Zn-O)</td>
<td>-</td>
<td>-</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>ν(Pt-C)</td>
<td>-</td>
<td>-</td>
<td>470</td>
<td></td>
</tr>
</tbody>
</table>

s – symmetric, a – asymmetric, b – bend, ν – stretch, δ – deformation, ρ – rock, γ – wag, χ – scissor

Heating to 200 K to desorb physisorbed anisole caused only minor changes in the HREEL spectrum including an increase in the intensity of the out-of-plane γ(C-H)ring peak
at 820 cm\(^{-1}\), diminution in the intensity of the in-plane \(\delta(C-H)\)\(_{\text{ring}}\) peak at 1010 cm\(^{-1}\), and disappearance of the peak at 1250 cm\(^{-1}\) which is likely due to both \(\nu(C-\text{OMe})\) and in-plane \(\nu(C-H)\)\(_{\text{ring}}\) modes. At such a low temperature it is unlikely that any chemical transformations of the adsorbed anisole have occurred; thus, these intensity changes must be due to the orientation of the chemisorbed anisole relative to the more random orientation for the physisorbed species. In particular, the decrease in the intensities of the peaks for in-plane modes relative to those for out-of-plane modes indicates that the aromatic ring is situated parallel to the surface in the chemisorbed species. This conclusion relies on the fact that an induced image dipole in the metal partially shields vibrational modes which have dipole moments parallel to the surface, thereby decreasing their HREELS cross-section. It is also consistent with DFT studies of the interaction of anisole with Pt(111) reported by Bonalumi et al. [107, 108] which showed that the aromatic ring in anisole adsorsbs in the same bridge site in which benzene adsorbs on this surface [109]. In this configuration the O-CH\(_3\) group is slightly tilted away from the surface.

Further heating the anisole-dosed Pt(111) surface to 250 K and then 300 K led to significant changes in the HREEL spectrum. These include a large decrease in the intensity of the ring breathing mode at 780 cm\(^{-1}\), the further emergence of an intense peak at 825 cm\(^{-1}\) and smaller peaks at 1630 and 1750 cm\(^{-1}\). Changes were also observed in the C-H stretching region of the spectrum with the intensity of the \(\nu(C-H)\)\(_{\text{ring}}\) mode decreasing relative to that of the aliphatic \(\nu(C-H)\) mode at 2870 cm\(^{-1}\). These signify that reaction or decomposition of the adsorbed anisole has started to occur by 300 K. While it is difficult to unambiguously assign the spectrum at this temperature to specific specie(s), the large decrease in the intensity of the ring breathing mode and the change in the relative intensities
of the aromatic and aliphatic ν(C-H) modes suggests a loss of aromatic character for at least a portion of the adsorbed intermediates.

Even more dramatic changes occurred in the HREEL spectrum obtained upon heating the sample to 350 K. At this temperature the spectrum was dominated by an intense peak at 825 cm\(^{-1}\). Smaller peaks are also apparent at 470, 1750, 2000, and 2870 cm\(^{-1}\), as well as several poorly resolved peaks between 1000 and 1450 cm\(^{-1}\). The peak at 2000 cm\(^{-1}\) can be assigned to CO adsorbed in atop sites and indicates that some C-C bond cleavage has started to occur by this temperature. We also assign the peak at 1750 cm\(^{-1}\) to adsorbed CO but in bridging sites. While this is an unusually low frequency for bridging CO, previous studies have shown that co-adsorbed electron-donating molecules, such as benzene, can cause a significant decrease in the C-O stretching frequency by increasing the amount of back donation of \(d\)-electrons from the metal into the \(\pi^*\) anti-bonding orbitals of the adsorbed CO [93, 110]. We believe that something similar is happening here. The fact that this peak shifts to 1800 cm\(^{-1}\) upon heating to higher temperatures which causes complete decomposition of the anisole reactant is also consistent with this explanation. It is noteworthy that with the exception of these ν(CO) peaks, the HREEL spectrum at this temperature is nearly identical to that reported by Ihm and White for an oxocyclohexadienyl intermediate (C\(_6\)H\(_6\)O, 2,5-cyclohexadienone) that is formed by reaction of phenol on Pt(111) [111]. In that study it was shown that this species bonds to the surface in an \(\eta^5\)-\(\pi\) configuration. To further illustrate this similarity we collected HREEL spectra for a phenol-dosed Pt(111) surface and the spectrum obtained after heating to 400 K is included in the supplemental
information. We, therefore, propose that an oxocyclohexadienyl species is also formed via the reaction of anisole on Pt(111). The near disappearance of the characteristic aromatic C-H stretch near 3000 cm\(^{-1}\) is also consistent with this conclusion. We also note that the \(\nu(C-O)\) mode

Formation of an oxocyclohexadienyl intermediate requires cleavage of the O-CH\(_3\) bond in anisole and the addition of an H atom to the ring. The O-CH\(_3\) bond cleavage would also produce adsorbed methyl groups. Previous studies of the interaction of methyl groups with Pt(111) show that they are unstable on this surface above 230 K and undergo dehydrogenation to produce adsorbed C and H \[112\]; thus, the desorption-limited H\(_2\) peak at 350 K in the TPD data in Figure 5.1. can be attributed to the H formed by this dehydrogenation reaction. The peak at 470 cm\(^{-1}\) in the HREEL spectrum that appears after heating to 350 K can be assigned to a Pt-C stretch of the associated carbon atoms.

Heating the anisole-dosed Pt(111) sample above 350 K caused the gradual disappearance of the vibrational peaks associated with adsorbed hydrocarbon intermediates with the peaks for adsorbed CO persisting up to 500 K. This result along with the simultaneous H\(_2\) and CO peaks at 480 K in the anisole TPD data (Figure 5.1) indicate that the oxocyclohexadienyl intermediate undergoes unselective decomposition near this temperature. This would produce small CH\(_3\) fragments that apparently undergo further dehydrogenation at higher temperatures giving rise to the broad H\(_2\) desorption feature between 550 and 750 K.
The HREELS data do not provide much insight into the origin of the 420 K CO peak in the anisole/Pt(111) TPD data. We can speculate, however, to its origin. It is possible that cleavage of either C-O bond in adsorbed anisole may occur. As discussed above, O-CH₃ bond cleavage results in the formation of oxocyclohexadienyl as indicated by HREELS. In contrast, cleavage of the Ph-O (Ph = phenyl group) bond would produce an adsorbed phenyl group and an adsorbed methoxy group. At the temperature at which this reaction occurs it is likely that the methoxy group would rapidly decompose which could give rise to the 420 K desorption-limited CO peak. Decomposition of the phenyl group could contribute to the higher temperature H₂ desorption features. The reaction pathways for anisole on Pt(111) as determined from the TPD and HREELS data are summarized in Figure 5.3.
Figure 5.4: TPD spectra obtained following exposure of the Zn/Pt(111) surface to 0.6 L of anisole.

5.3.2 Reaction of anisole on Zn/Pt(111)

Consistent with our previous studies of the reactivity of Zn-decorated Pt(111) surfaces [80, 100], adding 0.2 ML of Zn adatoms to the Pt(111) surface significantly altered its reactivity towards anisole. TPD data obtained from 0.2 ML Zn/Pt(111) dosed with 0.6 L of anisole are displayed in Figure 5.4. For this surface in addition to anisole, H₂ and CO, a range of other products were detected including CH₄, CH₂O, and C₂H₆. The low-temperature anisole desorption features were similar to those obtained from Zn-free Pt(111). Hydrogen primarily desorbed in two peaks centered at 450 and 500 K, and CO in a single peak at 500 K. Note that the large H₂ peak at 350 K for Pt(111) is nearly absent.
for Zn/Pt(111), and the onset of the primary H\textsubscript{2} and CO desorption features occurs at significantly higher temperatures (>100 K) on the Zn-modified surface. This indicates that Zn addition decreases the activity for C-H and C-C bond scission resulting in the adsorbed species derived from anisole being more stable on the Zn-modified surface. The observation of additional products from Zn/Pt(111) also indicates that the reactions on this surface are more selective. The CH\textsubscript{2}O produced at 445 K likely results from cleavage of the Ph-O bond followed by dehydrogenation of the resulting methoxide group. Note that during methanol TPD on Zn/Pt(111), CH\textsubscript{2}O is also produced near 445 K and previous studies have shown that this is a desorption-limited product [95]. Thus, in the case of anisole, Ph-O bond cleavage must occur below 445 K. Note that the Ph-O bond cleavage would also produce an adsorbed phenyl group and hydrogenation of this species could account for the small amount of benzene produced at 450 K.

HREEL spectra as a function of temperature for anisole-dosed Zn/Pt(111) are displayed in Figure 5.5. As expected, at temperatures below 190 K the spectrum is nearly identical to that obtained in this temperature range for Zn-free Pt(111) and is consistent with IR and Raman spectra for anisole (see Table 5.1) [104-106]. Heating to 215 K, which is sufficient to desorb physisorbed anisole, caused some changes including the emergence of a small peak at 400 cm\textsuperscript{-1}, a large increase in the intensity of the \(\delta\text{(C-H)}\)\textsubscript{ring} peak at 1000 cm\textsuperscript{-1}, and a decrease in the intensities of the \(\nu\text{(C-H)}\) peaks at 2880 and 3000 cm\textsuperscript{-1}. The peak at 400 cm\textsuperscript{-1} is at a position typically observed for metal-oxygen stretching modes [95, 113-115]. In our previous study of the reaction of methanol on Zn/Pt(111), methoxide groups adsorbed on Zn sites also had a \(\nu\text{(Zn-O)}\) stretch at this energy. This indicates that some adsorbed anisole binds to Zn sites on the surface via the oxygen.
Figure 5.5: HREEL spectra as a function of temperature for Zn/Pt(111) dosed with 0.6 L anisole at 115 K.
Comparing the HREEL spectra for adsorbed anisole obtained near 200 K for both the Pt(111) and Zn/Pt(111) surfaces reveals that there is prominent peak at 1000 cm\(^{-1}\) in the spectrum from Zn/Pt(111) which is nearly absent in that from Pt(111). This peak is at the expected position for the in-plane \(\delta(C-H)_{\text{ring}}\) mode of anisole. As discussed above, the absence of this in-plane mode in the Pt(111) spectrum at 200 K can be attributed to the aromatic ring being situated nearly parallel to the surface. In the case of Zn/Pt(111) the intensity of this peak indicates that the ring is tilted away from this surface. Note that this conclusion is consistent with what we have reported previously for the interaction of benzaldehyde with Pt(111) and Zn/Pt(111) surfaces [100]. Thus, based on the HREEL spectroscopy we propose that on Zn/Pt(111) anisole adsorbs via the oxygen as shown in Figure 5.3, with the phenyl ring tilted away from the surface.

When the anisole-dosed Zn/Pt(111) surface was heated to 250 K, only minor changes occurred in the HREEL spectrum including further increases in the intensities of the peaks at 400 and 1000 cm\(^{-1}\) and a change in the relative intensities of the aliphatic and aromatic \(\nu(C-H)\) peaks between 2800 to 3100 cm\(^{-1}\). Also note that the high intensity of the peak at 1000 cm\(^{-1}\) relative to the other peaks suggests that modes in addition to the in-plane \(\delta(C-H)_{\text{ring}}\) mode of anisole are contributing to this peak. Since C-O stretches of alkoxide groups are relatively intense and typically located near this energy [113-117], we propose that the \(\nu(C-O)\) mode of methoxide groups formed via cleavage of the Ph-O bond in a portion of the adsorbed anisole contributes to the peak at 1000 cm\(^{-1}\). This reaction would also produce an adsorbed phenyl group.

Heating the sample to 300 and then 350 K produced additional changes with the HREEL spectrum becoming dominated by the peaks at 400 and 1000 cm\(^{-1}\) and all the other
peaks becoming less intense. A small $\nu$(C-O) stretch at 2000 cm$^{-1}$ also grows in which may be due in part to adsorption of some CO from the background. It is noteworthy that the spectrum at this temperature is nearly identical to that reported for methoxide groups adsorbed on this surface [95] which further supports the conclusion that C-O bond cleavage has occurred producing adsorbed methoxide. The persistence of the characteristic aromatic $\nu$(C-H) peak at 3000 cm$^{-1}$, however, indicates that phenyl groups remain on the surface. At least a portion of these phenyl groups react to produce benzene that desorbs at 450 K as observed in the TPD data. Additional heating to 450 K resulted in the disappearance of the peaks associated with adsorbed hydrocarbon intermediates and the growth of the $\nu$(C-O) stretch at 2000 cm$^{-1}$ due to adsorbed CO.

The HREELS results for Zn/Pt(111) provide strong evidence for selective cleavage of the Ph-O bond in anisole to produce adsorbed methoxide and phenyl. While cleavage of the O-CH$_3$ bond in at least a portion of the absorbed anisole cannot be completely ruled out, the HREELS data do not provide any evidence for phenoxide or the oxocyclohexadienyl intermediate that was formed on the Zn-free Pt(111). As noted above, we have previously studied the reaction of CH$_3$OH on Zn/Pt(111) and in that study it was observed that methoxide groups formed by dissociative adsorption of methanol also reacted to form CH$_2$O which desorbed 440 K [95]. XPS and HREELS results indicated that the methoxide groups involved in this reaction were adsorbed on Zn sites. Methanol TPD data as a function of Zn coverage also showed that the area of the 440 K CH$_2$O peak went through a maximum near 0.4 ML of Zn and disappeared for Zn coverages greater than 0.8 ML indicating that the initial dissociative adsorption of CH$_3$OH does not occur directly on the Zn sites, but rather on adjacent Pt sites whose electronic properties are modified by Zn.
adatoms. As has been shown in several previous studies [39, 80, 81, 100], Pt-Zn interactions decrease the activity of the Pt surface for C-C and C-H bond activation resulting in adsorbed oxygenate and hydrocarbon intermediates being more stable on Zn-modified Pt compared to Zn-free Pt. Based on these previous results for methanol, we propose a similar scenario for the adsorption and reaction of anisole on Zn/Pt(111) with the initial chemisorption at low temperature occurring primarily on Pt sites adjacent to Zn adatoms. Selective cleavage of the Ph-O bond in these adsorbed anisole molecules produces methoxide groups that are bonded to the Zn atoms and phenyl groups bonded to adjacent Pt sites. This reaction pathway is shown in Figure 5.3.

It is somewhat more difficult to account for the CO, CH4 and H2 products that desorb at 500 K from the anisole-dosed Zn/Pt(111) surface. The fact that these products are all produced at the same temperature indicates that they are reaction-limited and result from the decomposition of a common intermediate. While the HREELS data do not provide much insight into what this intermediate may be, it is possible that unselective decomposition of anisole occurs on non Zn-modified portions of the surface producing adsorbed hydrocarbon fragments that undergo further decomposition near this temperature.

5.3.3 Reactor Studies

The studies of the interaction of anisole with the model catalysts demonstrate that Zn addition to the Pt(111) surface affects reactivity in several ways, including altering the strength of the interaction of the phenyl ring with the surface, altering the barriers for C-H and C-C bond cleavage, and providing sites that are selective for C-O bond cleavage. On Zn-free Pt(111) there is a strong interaction between the phenyl ring and the surface resulting in a bonding geometry in which the ring is situated parallel to the surface. Anisole
adsorbed in this configuration undergoes C-O and C-H bond scission at low temperatures to produce oxocyclohexadienyl and methyl groups with the former ultimately decomposing to produce CO, H₂ and small CH₃ fragments. In contrast, on Zn-modified Pt(111) a different adsorption configuration and reaction pathway for anisole were observed. As has been reported previously in our benzaldehyde study [100], through an electronic interaction the Zn decreases the adsorption energy of the phenyl ring with the surface. This causes the preferred adsorption geometry to be one in which the phenyl ring is tilted away from the surface with bonding occurring primarily via the oxygen. Selective C-O bond scission in this species at or near Zn sites produces adsorbed phenyl groups and methoxide groups with the latter being bonded to the Zn sites. While cleavage of the O-CH₃ bond to produce phenoxide groups might also occur, the TPD and HREELS results did not provide direct evidence for this pathway. These reaction pathways are summarized in Figure 5.3.

Based on the results obtained from the model catalysts one can speculate as to how the reactivity of supported Pt and Pt-Zn catalysts may differ for the HDO of anisole. Since the reaction of anisole on Pt(111) was not found to be selective for C-O bond cleavage, one would not expect high surface area Pt catalysts to be particularly selective for the reaction of anisole to produce benzene or phenol. The adsorption configuration of anisole on Pt(111) in which the phenyl ring lays flat on the surface may also help facilitate hydrogenation of the ring under typical HDO reaction conditions where there is a high partial pressure of H₂. Thus, one might also expect Pt catalysts to produce ring hydrogenation products for these conditions which are generally undesired since aromatic compounds have higher values. Since modifying Pt(111) with Zn changes the bonding configuration of anisole to one in which the primary interaction is via the oxygen with the phenyl ring tilted away from the
surface, one would expect Pt-Zn catalysts to be less likely to promote ring hydrogenation under HDO conditions. The results obtained from Zn/Pt(1 1 1) also indicate that Zn provides sites that are selective for C-O bond cleavage as evidenced by the production of methoxide, as determined by HREELS, and benzene which was observed as product during TPD. These observations along with the fact that Zn addition appears to lower the activity of the Pt surface for C-C bond cleavage [39, 80, 100], suggests that high surface area Pt-Zn catalysts have some promise for the HDO of lignin-derived oxygenates to produce aromatic compounds.

Figure 5.6: Product distribution for reaction of anisole on different catalysts under typical HDO conditions: (A) 10 wt % Pt/C, W/F = 0.5 g·min/ml, (B) 1 wt % Pt/C, W/F = 0.1667 g·min/ml, (C) 10 wt % PtZn/C, W/F = 0.5 g·min/ml, at 598 K and 27.5 bar.

In order to verify these predictions from the model catalyst results, we evaluated the performance of carbon-supported Pt and Pt-Zn catalysts for HDO of anisole using a tubular
flow reactor. Details of the catalyst synthesis and reactor configuration are given in the experimental section. Conversion and product distributions for Pt/C and PtZn/C catalysts at a reaction temperature of 598 K are shown in Figure 5.6. Note that only the condensable products were collected and analyzed and no ring opening products were detected. Also note that in addition to the products listed, some methane was likely produced.

As shown in Figure 5.6, at a space time of 0.5 g·min⁻¹·ml⁻¹ the anisole conversion over 10 wt % Pt/C was 75 % with a high selectivity to methoxycyclohexane which made up 74 % of the condensable product. Smaller amounts of demethylation products, cyclohexane and cyclohexanol, were also produced. In order to determine the product selectivity at lower conversion (i.e. closer to differential reaction conditions) and to determine if any other intermediate products were produced, experiments were also performed for a 1 wt % Pt/C catalyst with a reactant space time of 0.17 g·min⁻¹·ml⁻¹. For these conditions the anisole conversion was only 31 % but the selectivity to methoxycyclohexane increased to 88 % and only small amounts of demethylation products, cyclohexane, cyclohexanone, and cyclohexanol, were produced. Using these data and an average Pt particle size as determined by TEM, the turnover frequency (TOF) for these reaction conditions is estimated to be 0.22 s⁻¹. This value is similar to that reported previously, 0.104 s⁻¹, for the gas phase HDO of anisole over a Pt/SiO₂ catalyst [101]. The increase in methoxycyclohexane selectivity with decreasing space time at the expense of the products requiring demethylation suggests that demethylation occurs after ring hydrogenation. Thus, on the Pt/C catalyst hydrogenation of the phenyl ring appears to be rather facile. This observation is consistent with the model catalyst studies which demonstrated an adsorption configuration for anisole on Pt(111) that would facilitate its hydrogenation, namely
bonding via the \( \pi \)-orbitals of the phenyl ring with the ring lying flat on the surface. Thus, as predicted by the model catalysts studies, Pt/C has high activity for ring hydrogenation and low activity for selective C-O bond scission.

The conversion and product selectivity data for the 10 wt % PtZn/C catalyst at a reactant space time of 0.5 g·min⁻¹·ml⁻¹ are also presented in Figure 5.6. These data show that, as expected, alloying Pt with Zn significantly alters reactivity. The PtZn/C catalyst has lower overall activity with the anisole conversion being less than half that obtained for Pt/C at similar reaction conditions (corresponding to a TOF of 0.013 s⁻¹ which was estimated assuming the same average particle size as the Pt/C catalyst). The PtZn/C catalyst is also highly selective for the production of phenol which represented 66% of the condensable product. Products requiring phenyl ring hydrogenation were also produced, most notably cyclohexane and cyclohexanol, but accounted for only ~27% of the condensable products.

It is likely that the co-impregnation method used to synthesize the Pt-Zn catalyst would produce metal particles with a range of Pt:Zn ratios. Since the Pt/C catalyst was highly active for phenyl ring hydrogenation it is possible that for the PtZn/C catalyst the ring hydrogenation products were produced on Pt-rich particles. To investigate this possibility and to assess the effect of Zn content on reactivity, reactor studies were also performed for a 10 wt % PtZn₃/C catalyst which had a Pt:Zn ratio of 1:3. Conversion and product selectivity data as a function of reaction temperature for this catalyst are presented in Figure 5.7 (\( W/F = 0.5 \) g·min⁻¹·ml⁻¹, \( P(H_2) = 27.5 \) bar). These data show that increasing the Zn content dramatically decreased overall activity with only 10% conversion at 598 K, but increased the selectivity to phenol to nearly 91%. Increasing the temperature to 623 and 648 K resulted in an increase in conversion but the high selectivity to phenol was
maintained. These results support the possibility that in the case of the Pt-Zn catalyst the ring hydrogenation products were produced on Pt-rich particles.

![Graph showing product distribution](image)

Figure 5.7: Product distribution for reaction of anisole on PtZn/C catalyst as a function of temperature. W/F = 0.5 g\(^*\)min/ml, 27.5 bar

It is important to note that while selective C-O bond scission was observed for both the model and high surface area PtZn catalysts, a different C-O bond was cleaved in each case. On Zn/Pt(111) cleavage of the Ph-O bond resulted in the production of benzene, while PtZn/C was selective for the less-desirable cleavage of the O-CH\(_3\) bond leading to the production of phenol. The origin of this discrepancy is not clear, but the disparate reaction conditions between the UHV and reactor studies, \textit{i.e.} presence of a solvent (\textit{n}-heptane) and a high pressure of H\(_2\) in the case of the reactor studies, may have played a role. The surface structures of the model and high surface area catalysts are also likely to be much different. Nonetheless, it is interesting that in both cases the addition of Zn increases the selectivity
for C-O bond cleavage and based on the model catalyst studies this appears to be due to surface Zn atoms providing a binding site for the oxygen in the anisole reactant.

4.7 Conclusion

The combined surface science and reactor studies provide considerable insight into both the reactivity of aromatic oxygenates on Pt and how alloying with a second more oxyphilic metal, such as Zn, can be used to alter the reactivity and increase the selectivity for C-O bond cleavage which is required for HDO of this class of molecules. As described in the introduction, previous studies have suggested that alloying Pt with a more oxyphilic metal decreases the strength of the interaction of aromatic rings with the Pt surface [83-85]. The results obtained here show this quite dramatically for anisole where binding on Pt(111) occurs primarily via the π-orbitals of the phenyl ring with the ring situated parallel to the surface, while on Zn-modified Pt(111) the ring is tilted away from the surface and bonding occurs primarily via the oxygen lone pair electrons on a surface Zn site or possibly an adjacent Pt site. The reactor studies show that this difference in bonding geometry and adsorption sites has a significant effect on reaction selectivity. In particular the bonding geometry on Pt facilitates hydrogenation of the phenyl ring and the Pt/C catalyst exhibited high selectivity to saturated products, such as methoxycylohexane and cyclohexane. In contrast on PtZn catalysts for which the model catalyst studies suggested that the phenyl ring will have limited interaction with the surface, ring hydrogenation was greatly suppressed with the primary reaction product being phenol.

The alteration of the interaction of the aromatic rings with the Pt surface appears to be largely an electronic effect of alloying with Zn. The results obtained here and in our
previous studies [39, 80, 81, 100], however, also show that the oxyphilic nature of the Zn makes it the preferred binding site for oxygen and an active site for selective C-O bond cleavage. This was shown for the Zn/Pt(111) model catalyst where Zn-bound methoxide was observed as a primary reaction intermediate and for the high surface area PtZn/C catalysts which exhibited high selectivity to phenol. Apart from the specific case of PtZn which was investigated here, we believe the results of this study are more generally applicable and help explain why a range of bimetallic catalysts composed of a group 10 metal and a second more oxyphilic metal, e.g. PdZn, PdFe, NiFe, and PtSn [24-27], exhibit promising characteristics as catalysts for the HDO of lignin-derived oxygenates to produce high-value aromatic compounds.
Chapter 6  TPD and HREELS Study for the Reaction of Guaiacol on Zn-Decorated Pt(111)\textsuperscript{4}

Summary

Temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) were used to characterize the adsorption and reaction of guaiacol on Pt(111) and Zn-modified Pt(111) surfaces. It was found that the guaiacol molecule binds to the Pt(111) surface via the aromatic ring which facilitates unselective decomposition to produce CO, H\textsubscript{2} and small hydrocarbon fragments at relatively low temperatures. In contrast, on Zn-modified Pt(111) surfaces, guaiacol was found to bond to surface Zn sites via the oxygen atoms in the molecule producing a bonding configuration in which the aromatic ring is tilted away from the surface. Such a binding configuration facilitates the desired C-O bond cleavage while keeping the aromatic nature of the molecule intact.

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5.1 Introduction

Lignocellulosic biomass is attracting more and more attention as a potentially sustainable, CO₂-neutral feedstock for fuels and chemicals [11, 14, 96]. The polyaromatic nature of the lignin fraction of biomass also makes it an attractive feedstock for aromatic compounds [11, 79]. Currently, the most prevalent conversion technology for lignin relies on pyrolysis [11], which produces bio-oil, biochar, and synthesis gas as products. The bio-oil is a complex mixture of phenolic compounds and lignin-derived oligomers with high oxygen content [118]. It also contains 15-30% water. The bio-oil tends to have high viscosity, high acidity, low stability, as well as low heating value. Therefore, further upgrading of the bio-oil is needed in order to form useful products. Removal of some of the oxygen via hydrodeoxygenation (HDO) is an important step in the upgrading process, although this needs to be done while maintaining the aromatic nature of the constituent molecules in order to produce high-value products.

Selective hydrogenolysis of C-O bonds is the key step in the HDO upgrading of lignin-derived biomolecules. Recently there has been a number of studies reported in the literature on the use of group 10 metals, such as Pt [24, 46, 119-121], Pd [24, 121, 122], and Ni [122], as catalysts for this reaction. While all of these metals are active for C-O bond hydrogenolysis, they also promote the undesirable hydrogenation of aromatic rings and tend to deactivate due to coking. Alloying these group 10 metals with a more oxyphilic metal, such as Fe [24], Sn [26], or Zn [123] has been shown to be a promising strategy for designing more selective catalysts that maintain activity for C-O bond hydrogenolysis while simultaneously having low activity for ring hydrogenation. Insight into the
mechanism by which alloying with a more oxyphilic metal affects activity and selectivity, however, is only starting to emerge.

In previous studies we have investigated the adsorption and reaction of aromatic oxygenates that contain aldehyde (benzaldehyde)\cite{100} and alkoxide (anisole)\cite{123} functionalities on model catalysts consisting of Pt(111) and Zn-decorated Pt(111) surfaces. These studies show that Zn addition to Pt alters the d-band of the metal in such a way that it decreases the binding of the aromatic group to the surface. These studies along with those for simpler oxygenates, such as methanol and acetaldehyde\cite{39,95}, also indicate that the Zn atoms provide bonding sites for the oxygen atoms in these molecules and that this may help facilitate selective cleavage of C-O bonds.

In the work described here we have expanded our previous investigations of the adsorption and reaction of lignin-derived model compounds on model catalysts consisting of Pt(111) and Zn-decorated Pt(111) surfaces\cite{100,123} to include guaiacol which contains both alkoxide and hydroxyl functionalities. Temperature-programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) were used to investigate reaction pathways and determine the bonding configurations of stable adsorbed intermediates formed from guaiacol. This study in conjunction with our previous work provide considerable new insight into how alloying a group 10 metal with a more oxyphilic metal, such as Zn, affects the reaction pathways, adsorbed intermediates, and active sites for C-O bond cleavage in aromatic oxygenates such as those found in pyrolysis oils produced from lignin.
5.2  Experimental

Both TPD and HREELS experiments were conducted in a UHV apparatus described in detail in previous publications [39, 64, 65]. The system was equipped with a quadruple mass spectrometer (SRS RGA200), an ion sputter gun (PHI electronics) and an HREEL spectrometer (LK Technologies) and had a background pressure of $2 \times 10^{-10}$ torr. A Pt(111) single crystal substrate which was 10 mm in diameter and oriented to within ±0.5° was spot-welded to two tantalum wires that were connected to the UHV sample manipulator. The Pt(111) surface was cleaned by repeated cycles of 2 kV Ar$^+$ ion bombardment at 600 K for 40 min, annealing at 1200 K under $2 \times 10^{-8}$ torr O$_2$ for 15 min, and annealing at 1200 K in vacuum for 5 min. The sample was heated resistively and cooled to 110 K by conduction from a liquid N$_2$ reservoir.

Zn deposition on Pt(111) was obtained by exposing the Pt surface to a beam of Zn atoms produced from a thermal evaporative source consisting of a coil of Zn wire (Alfa Aesa, 99.99%) around a resistively-heated tungsten filament. The Zn flux from this source was monitored using a quartz crystal microbalance (QCM) that was located midway between the source and the sample but positioned below the sample in order to not block the flux of atoms to the Pt crystal. One monolayer of Zn was assumed to have the same density of atoms as that on the Pt(111) surface, i.e., $1.51 \times 10^{15}$ atoms/cm$^2$.

In a previous study [57] it was shown that Zn atoms vapor deposited on Pt(111) remain on the surface at temperatures below 600 K, while at higher temperatures they diffuse into the surface where they form a substitutional alloy in which the Zn primarily resides in the second layer [57]. Since the goal of the present study was to assess how addition of Zn to Pt influences reactivity, both through electronic effects and by providing specific sites for
adsorption, we chose to use a Pt(111) surface decorated with Zn adatoms as a model PtZn alloy surface.

The guaiacol reactant (Sigma Aldrich, 99.8%) was contained in a glass vial attached to a stainless steel manifold that was connected to the main UHV apparatus via a variable leak valve that was equipped on the UHV side with a directional dosing tube. While dosing guaiacol the sample was positioned directly in front of the dosing tube allowing a lower base pressure to be maintained for vacuum chamber. Based on previous calibration studies the dosing tube enhanced the reactant gas pressure at the sample surface by a factor of 10-fold relative to that measured in the vacuum chamber.

TPD experiments as a function of the guaiacol dose were performed for the Pt(111) surface in order to determine the dosage that resulted in saturation of the low-temperature guaiacol peak from the Pt(111) surface which corresponds to the desorption of second layer guaiacol. Based on these experiments it was determined that saturation of the surface with guaiacol occurred for a 0.5 L (1 L = 10^{-6} torr) dose and this dosage was used in all subsequent TPD and HREEL experiments. Note that this dose ensured that all the experiments in this study were done using surfaces that were completely saturated with chemisorbed guaiacol. A heating rate of 3 K/s was used in the TPD experiments and the HREEL spectra were collected using a 4 eV electron beam oriented at 60° with respect to the surface normal. The full width at half-maximum of the elastic peak obtained from the clean surface was typically 40 cm^{-1}. HREEL spectra were collected as a function of sample temperature. For temperatures greater than the dosing temperature the sample was heated at 3 K/s to the indicated temperature and then rapidly quenched to low temperature at which point the spectrum was collected.
5.3 Results and Discussion

6.3.1 TPD of guaiacol on Pt(111) and Zn/Pt(111) surfaces

TPD results for Pt(111) dosed with 0.5 L of guaiacol are displayed in the Figure 6.1. In addition to a narrow guaiacol peak at 225 K, which based on previous studies of similar aromatic molecules on Pt(111) can be assigned to desorption of second layer physisorbed species[111], the only other desorbing species were H\textsubscript{2} at 340 and 435 K, and CO at 435 K. The fact that the CO and H\textsubscript{2} peaks at 435 K occur at the same temperature and have similar shapes suggests that they are reaction-limited products of the decomposition of a common adsorbed intermediate. Since CO was the only carbon-containing reaction product this decomposition reaction must also result in carbon deposition on the surface. Assuming that all of the oxygen in the guaiacol reactant is accounted for in the CO product along with the 7:2 carbon-to-oxygen ratio in the guaiacol reactant, the TPD data indicate that roughly 2.5 carbon atoms were deposited on the surface for every CO molecule produced. The lower-temperature H\textsubscript{2} peak at 340 K is consistent with a desorption-limited process [124] and thus demonstrates that dehydrogenation of at least a portion of the adsorbed guaiacol must occur below this temperature.
Figure 6.1: TPD spectra obtained following exposure of the Pt(111) surface to 0.5 L of guaiacol (GUA).

For TPD studies of the reactivity of Zn modified Pt(111) surfaces a 0.4 ML Zn/Pt(111) surface was chosen as a representative model alloy surface. Consistent with our previous studies [80, 100], addition of Zn adatoms to the Pt(111) surface caused a significant change in reactivity. Figure 6.2 displays TPD data for a 0.4 ML Zn/Pt(111) surface dosed with 0.5 L of guaiacol. For this surface a narrow guaiacol peak at 225 K corresponding to physisorbed species is again observed. Other notable features are CO and H\textsubscript{2} peaks at 750 K indicating the decomposition of an adsorbed intermediate occurs at this temperature. Note that this is over 300 K higher than the corresponding peaks for the Zn-free surface demonstrating that Zn addition results in significant stabilization of the adsorbed species. Additional features in the TPD data include a smaller H\textsubscript{2} peak centered at 525 K and a small CH\textsubscript{4} desorption peak at 480 K. This latter peak indicates that scission of the C-O bond in the –O-CH\textsubscript{3} group in at least some of the adsorbed guaiacol occurs at or below this temperature. As was the case for Pt(111) these data also indicate that carbon is deposited
on the surface after a guaiacol TPD run. Quantification of the TPD data indicates that roughly 2.25 carbon atoms were deposited on the surface for every CO molecule produced (this again assumes all of the oxygen in the guaiacol reactant is accounted for in the CO product). The quantification of the TPD data also reveals that the saturation coverage of chemisorbed guaiacol on the Pt(111) was approximately 10% higher than that on and Zn/Pt(111). It is also noteworthy that Pt(111) surfaces covered with multilayers of Zn were found to be unreactive towards guaiacol, thus demonstrating that the chemistry observed for the 0.4 ML Zn/Pt(111) surface cannot be attributed completely to reaction on surface Zn sites.

Figure 6.2: TPD spectra obtained following exposure of the Zn/Pt(111) surface to 0.5 L of guaiacol (GUA). (These data are displayed on the same scale as those in Figure 6.1)
6.3.2 HREELS of guaiacol on Pt(111) and Zn/Pt(111) surfaces

HREEL spectroscopy was used to identify the stable surface intermediates and their reaction and interconversion as a function of surface temperature. HREEL spectra collected as a function of temperature for Zn-free and 0.4 ML Zn-Pt(111) surfaces with a 0.5 guaiacol dosage at 120 K are displayed in Figure 6.3 and Figure 6.5, respectively. For both the Zn-free and Zn-modified Pt(111) surfaces, the spectra at 150 K contain characteristic peaks of molecular guaiacol which can be assigned by comparison to the corresponding IR and Raman spectra \[125, 126\] of the free molecule. These peak assignments are presented in Table 6.1. Note that the characteristic peaks for guaiacol include the b(CCO) at 740 cm$^{-1}$, $\nu$(C-O) at 1250 cm$^{-1}$, $\nu$(C-H)$_{\text{methyl}}$ at 2870 cm$^{-1}$, $\nu$(C-H)$_{\text{ring}}$ at 3030 cm$^{-1}$ and a hydrogen bonded $\nu$(O-H) peak at 3300 cm$^{-1}$. 
Figure 6.3: HREEL spectra as a function of temperature for Pt(111) dosed with 0.5 L guaiacol at 115K.
Table 6.1: Vibrational mode assignment of guaiacol on Pt(111) and Zn/Pt(111) surface

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency cm⁻¹</th>
<th>IR/Raman [125, 126]</th>
<th>Pt (111)</th>
<th>Zn/Pt(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ring deformation (out-of-plane)</td>
<td>584,583</td>
<td>580</td>
<td>580</td>
<td></td>
</tr>
<tr>
<td>b (CCO) (out-of-plane)</td>
<td>741,727</td>
<td>740</td>
<td>730</td>
<td></td>
</tr>
<tr>
<td>γ (C-H)ring (out of plane mode)</td>
<td>823,859</td>
<td>830</td>
<td>840</td>
<td></td>
</tr>
<tr>
<td>b (CCH) (in-plane mode) + ν (O-Me)</td>
<td>1024,1027,1040</td>
<td>1010</td>
<td>1080</td>
<td></td>
</tr>
<tr>
<td>b (OCH) + b (CCH)ring (in-plane mode)</td>
<td>1156,1157,11173,1172</td>
<td>-</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>ν (C-OMe)+ν (C-OH)</td>
<td>1225,1261</td>
<td>1250</td>
<td>1250</td>
<td></td>
</tr>
<tr>
<td>b (HCH)</td>
<td>1444,1443,1458,1454</td>
<td>1430</td>
<td>1430</td>
<td></td>
</tr>
<tr>
<td>ν (C-C)ring (in plane mode)</td>
<td>1502,1597</td>
<td>1550</td>
<td>1560</td>
<td></td>
</tr>
<tr>
<td>ν (C-H)methyl</td>
<td>2840,2950,2965</td>
<td>2870</td>
<td>2870</td>
<td></td>
</tr>
<tr>
<td>ν (C-H)ring</td>
<td>3052</td>
<td>3030</td>
<td>3030</td>
<td></td>
</tr>
<tr>
<td>ν(O-H)</td>
<td>-</td>
<td>-</td>
<td>3500</td>
<td></td>
</tr>
<tr>
<td>ν(O-H) (hydrogen bonded)</td>
<td>3330</td>
<td>3300</td>
<td>3350</td>
<td></td>
</tr>
<tr>
<td>ν (Pt-O)</td>
<td>-</td>
<td>505</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ν (Zn-O)</td>
<td>-</td>
<td>-</td>
<td>425</td>
<td></td>
</tr>
<tr>
<td>ν (Pt-C)</td>
<td>-</td>
<td>450</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

s – symmetric, as – asymmetric, b – bend, ν – stretch, δ – deformation, ρ – rock, γ – wag, χ – scissor

As shown in Figure 6.3, heating the guaiacol-dosed Pt(111) surface to 225 K caused several changes in the HREEL spectrum of the adsorbed species. Since heating to this temperature is sufficient to desorb any weakly-bound guaiacol (see Figure 6.1), this spectrum corresponds to chemisorbed species. One subtle change that occurred upon heating is a small decrease in the intensities of the peaks for the in–plane modes between 900 and 1600 cm⁻¹ relative to that of the prominent CCO out-of-plane bending peak at 740 cm⁻¹. In our previous studies of the adsorption of benzaldehyde and anisole on Pt(111) [100, 123], similar changes in the HREEL spectra that occurred upon heating to desorb weakly-bound species could be attributed to a bonding configuration of the chemisorbed molecule in which the aromatic ring is situated parallel to the surface. Due to induced image dipoles in the metal, this configuration causes a decrease in the intensities of the in-plane vibrational modes. While an analysis of the changes in the relative intensities of the
vibrational peaks for adsorbed guaiacol is less clear on this point, previous DFT studies indicate that a binding configuration in which the aromatic ring in guaiacol is parallel to the Pt(111) surface is also the most energetically favorable [127, 128]. Other more prominent changes in the spectrum upon heating to 225 K include the emergence of an intense peak at 610 cm\(^{-1}\) and the disappearance of the broad \(\nu\)(O-H) peak between 3200 and 3600 cm\(^{-1}\). This latter peak was broad in the 150 K spectrum due to hydrogen bonding in the physisorbed multilayer and it is notable that it was not replaced by a distinct \(\nu\)(O-H) peak in the OH stretching region of the spectrum. A change in the relative intensities of the aromatic and aliphatic \(\nu\)(C-H) peaks at 3030 cm\(^{-1}\) and 2870 cm\(^{-1}\), respectively, is also apparent, with that of the aliphatic peak increasing relative to that of the aromatic peak.

Together all of these changes indicate that the guaiacol has undergone some reaction upon heating to 225 K. Unfortunately based on the HREEL spectrum alone it is not possible to definitively determine the structure of the adsorbed intermediate(s) at this temperature. The intense peak at 610 cm\(^{-1}\) is particularly difficult to assign, although a \(\delta\)(CCO) mode is one possibility [39]. It is noteworthy, however, that in previous studies of the reactions of phenol and anisole on Pt(111) [111, 123], cyclohexadienone was identified as an adsorbed intermediate and this species exhibited an HREEL spectrum that shares features similar to that observed here for guaiacol-dosed Pt(111) at 225 K. Thus, it is likely that the guaiacol reacts on Pt(111) to form the analogous 2-methoxy-2,5-cyclohexadien-1-one. The structure of this species is shown in Figure 6.4, as well as a possible surface bonding configuration in which the ring is parallel to the surface.
Heating the surface to 285 K caused several more prominent changes in the spectrum of the adsorbed species including the disappearance of the intense peaks at 610 and 740 cm\(^{-1}\), the emergence of a series of new peaks between 800 and 1200 cm\(^{-1}\), and the disappearance of the \(\nu(CH)_{ring}\) peak at 3030 cm\(^{-1}\) as well as the ring out-of-plane \(b(CCO)\) peak at 740 cm\(^{-1}\). These latter two changes indicate the loss of the aromatic character of the adsorbed species. While we are not able to definitively assign this spectrum to a specific adsorbed intermediate(s), these changes clearly show that significant decomposition of the adsorbed guaiacol has occurred by this temperature. This is consistent with the TPD results which show H\(_2\) desorption commencing at 280 K.

Spectra obtained after heating to higher temperatures provides additional evidence for unselective decomposition of the adsorbed guaiacol on Pt\((111)\). At 485 K the spectrum is dominated by peaks at 1800 and 2000 cm\(^{-1}\) corresponding to the \(\nu(C-O)\) modes of CO adsorbed in bridge and atop sites, respectively. The C-H stretch at 2870 cm\(^{-1}\), the series of small peaks between 600 and 1500 cm\(^{-1}\), and the emergence of a peak at 450 cm\(^{-1}\), which
can be assigned to C-Pt stretch, all indicate that some hydrocarbon fragments are also present on this surface at this temperature.

HREELS data as a function of temperature for a guaiacol on a Zn-modified Pt(111) surface are displayed in Figure 6.5. A 0.4 ML Zn coverage was selected here as a representative Zn adatom surface. The spectra were again obtained after saturating the surface with 0.5 L guaiacol at 150 K and then briefly heating to the indicated temperatures. As noted above, at 150 K the spectrum is similar to that obtained for this temperature from the Zn-free Pt(111) and is consistent with the IR and Raman spectrum of molecular guaiacol (see Table 6.1) [125, 126]. Heating to 215 K to desorb the weakly bound physisorbed guaiacol produced relatively few changes in the spectrum. Indeed, the spectrum of the adsorbed species is remarkably similar for annealing temperatures between 215 and 450 K, although some subtle differences are observed. It is particularly noteworthy that the $\nu(C-H)_\text{ring}$ peak at 3030 cm$^{-1}$ remained unchanged up to 450 K, demonstrating that the aromatic ring remains intact up to this temperature. This is in stark contrast to what was observed for the Zn-free Pt(111) surface where complete loss of the aromatic character of the adsorbed species occurred by 285 K.
Figure 6.5: HREEL spectra as a function of temperature for Zn/Pt(111) dosed with 0.5 L guaiacol at 115K.
One change that is apparent upon heating from 215 to 300 K is the disappearance of the O-H stretching peak at 3500 cm\(^{-1}\). A small but distinct peak also emerges at 425 cm\(^{-1}\) in this temperature range. Based on our previous studies of Zn-modified surfaces [95, 123] we assign this latter feature to a \(\nu(\text{Zn-O})\) stretching mode. Meanwhile, some minor changes in the relative intensities of the ring in-plane and out-of-plane vibrational modes were also observed upon heating to 300 K; however, unlike the case of Zn-free Pt(111), no significant diminution of the in-plane modes was observed, indicating that the aromatic ring is tilted away from the Zn-modified surface. Previous studies of the adsorption of other aromatic oxygenates on Pt(111) surfaces, such as benzaldehyde and anisole, have also reported that Zn addition to the surface results in bonding configurations in which the aromatic ring is tilted away from the surface [100, 123]. Together these changes indicate that the O-H group in guaiacol undergoes dissociation on Zn/Pt(111) at temperatures below 300 K with bonding of the hydroxyl oxygen most likely occurring at a Zn site as shown schematically in Figure 6.4. The conclusion that the oxygen binds to Zn sites is also consistent with previous studies in which it was shown by XPS that methanol adsorbs via the oxygen on Zn sites on Zn/Pt(111) [95].

Additional changes observed in the HREEL spectra upon heating the guaiacol-dosed Zn/Pt(111) surface to 450 K and above, include the disappearance of the \(\nu(\text{C-H})_{\text{methyl}}\) peak at 2870 cm\(^{-1}\) as well as the emergence of a small peak at 2000 cm\(^{-1}\), which is indicative of the \(\nu(\text{C-O})\) mode of adsorbed atop CO species. It is possible that this latter peak is due to adsorption of some CO from the chamber background. A gradual decrease in the intensity of the peak at 1010 cm\(^{-1}\), which is due primarily to the \(\nu(\text{O-Me})\) stretch, is also observed upon heating to 450 K. We propose that this results from cleavage of the O-Me bond in at
least a portion of the adsorbed species. This scenario is consistent with the TPD results which show the production of CH$_4$ as a primary product starting at 400 K. It is likely that this C-O bond dissociation reaction also involves an oxyphilic Zn site (see Figure 6.4), although we have no direct evidence for this.

Figure 6.4 shows a schematic of a proposed reaction pathway for guaiacol on Zn/Pt(111) that is consistent with our TPD and HREELS data. The added Zn alters the electronic properties of the surface that causes a decrease in its interaction with the aromatic ring and guaiacol interacts with Zn/Pt(111) primarily through the O atoms with dissociation of the O-H group occurring below 300 K at a Zn site. This is followed by O-CH$_3$ bond cleavage which occurs between 300 and 450 K. A proposed transition state for this reaction is shown in Figure 6.4 in which the methoxide O bonds to a Zn site and the methyl carbon bonds to an adjacent Pt site. This reaction produces a catechol-like intermediate bonded via the oxygens to Zn sites. This conclusion is consistent with previous studies that have reported catechol as one of the products produced during the HDO of guaiacol over bimetallic catalyst such as Pd-Fe [24] and Pt-Sn [26]. This intermediate is stable on the surface to temperatures in excess of 550 K. A similar pathway and active sites has been reported for -O-CH$_3$ bond cleavage in adsorbed anisole on Zn/Pt(111) [123].

The HREELS results together with the TPD data vividly demonstrate that Zn addition results in significant stabilization of adsorbed guaiacol on the Pt(111) surface. This is consistent with previous studies of the reaction of aldehydes and biomass-derived oxygenates on Zn-modified Pt surfaces where it has been shown that Zn addition decreases the activity of the Pt(111) surface for both C-C and C-H bond cleavage [39, 80, 100, 123], while simultaneously facilitating C-O bond cleavage. While not investigated here, the
weakening of the interaction of the aromatic ring with the Pt(111) surface upon Zn addition resulting in the ring tilting away from the surface would also likely decrease the propensity of the ring to become hydrogenated under typical hydrodeoxygenation reaction conditions. Since ring hydrogenation is usually undesirable this could be another positive attribute of PtZn catalysts.

5.4 Conclusions

This study provides useful insight into the adsorption and reaction of the lignin-derived oxygenate, guaiacol, on Pt(111) and Zn-modified Pt(111) surfaces. For Zn-free Pt(111), guaiacol interacts with the surface via the π-orbitals of the aromatic ring with the ring situated parallel to the surface. Such binding configuration promoted unselective decomposition with loss of the aromatic character of the ring occurring at temperatures as low as 225 K. Modifying the Pt(111) surface with Zn adatoms, however, was found to significantly alter the binding configuration of guaiacol. On this surface the aromatic ring interacted less strongly with the surface and the guaiacol molecule underwent dissociative adsorption at the hydroxyl group with bonding to the surface occurring primarily via this oxygen at a Zn site with the aromatic ring tilted away from the surface. Such a binding configuration facilitated -O-CH₃ bond cleavage and would likely limit hydrogenation of the ring under typical HDO reaction conditions.
Chapter 7  Mechanistic Study of the Hydrodeoxygenation of Lignin-derived Oxygenates on a PtCo Bimetallic Catalyst: Reaction of Anisole on Co-modified Pt(111)\textsuperscript{5}

Summary

Temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) were used to characterize the adsorption and reaction of anisole (C\textsubscript{6}H\textsubscript{5}-OCH\textsubscript{3}) on Pt(111) and Co-decorated Pt(111) surfaces. On both surfaces anisole was found to undergo O-CH\textsubscript{3} bond cleavage to form an oxocyclohexadienyl-structured intermediate (C\textsubscript{6}H\textsubscript{6}O) which bonds to the surface in a η\textsuperscript{5}-π configuration. Interaction of the O atom in this intermediate with Co adatoms was found to facilitate selective cleavage of the C-O bond to produce adsorbed benzene or phenyl groups. In parallel with this pathway, unselective decomposition of adsorbed anisole was also found to occur. The results obtained in this study along with those previously reported for the reaction of anisole on Zn-decorated Pt(111) surfaces provide further insight into how the addition of a second more oxyphilic metal to Pt affects surface reaction pathways and the hydrodeoxygenation (HDO) selectivity of lignin-derived aromatic oxygenates.

\textsuperscript{5} This chapter was submitted to Journal of Physics: Energy
7.1 Introduction

There has been a growing interest in the development of technologies that use renewable resources, such as lignocellulosic biomass, as an alternative to fossil-based resources as feedstocks for the production of a range of fuels and chemicals [16, 59, 60]. While much effort has focused on methods for upgrading the cellulose and hemicellulose fractions of biomass, especially for the production of hydrocarbon-based fuels [3, 77], until recently utilization of the lignose fraction has received much less attention. While the highly branched, polyphenolic nature of lignin makes it more refractory and, therefore, more difficult to process compared to cellulose, these same properties make it an attractive feedstock for a range of high-value aromatic compounds [11, 79]. The constituent, substituted aromatic molecules that are produced by lignin depolymerization via pyrolysis or other means also generally require additional processing. In particular, the presence of oxygenated substituents on the aromatic rings make hydrodeoxygenation (HDO) an important step in the overall upgrading process [3, 11].

While supported group 10 metals (i.e. Ni, Pd, Pt) are known to be active HDO catalysts, they also have high activity for the hydrogenation of aromatic rings leading to less-desirable saturated ring products when used for the HDO of lignin-derived aromatic oxygenates [44, 48, 98, 99]. Alloying a group 10 metal with a second oxyphilic metal such as Fe or Zn [24-27] has emerged as a promising approach to overcome this problem and such catalysts show higher HDO selectivity to the desired aromatic products. In order to understand the mechanism by which the addition of the oxyphilic metal affects the overall catalyst HDO activity and selectivity our group has undertaken a series of mechanistic studies of the reaction of lignin-derived aromatic oxygenates, including benzaldehyde,
anisole, and guaiacol, on PtZn model catalysts consisting of a Pt(111) surface decorated with Zn adatoms [100, 123, 129]. These studies have revealed that the Zn additive has multiple effects including providing a binding site for the oxygen atoms in the reactant molecules which helps facilitate selective C-O bond cleavage. The Zn also has a longer range electronic effect that destabilizes the bonding of phenyl rings to the Pt surface. This destabilization is sufficient to change the bonding configuration of phenyl compounds on Pt(111) from one where the ring lays flat on the surface to one where it is tilted away from the surface. We have argued that this change in bonding configuration is responsible for the decrease in the ring hydrogenation activity of PtZn compared to Pt alone.

While our previous studies have provided considerable insight into how Zn alters the HDO activity of Pt, it is not clear how general these observations are and if the addition of other oxyphilic metals to Pt will have a similar effect. Cobalt is another oxyphilic metal that has been used to modify the HDO activity of Pt. Previous studies [38, 130-132], however, provide a somewhat contradictory picture of the effect of Co addition. For example, in experimental and theoretical studies of the HDO of both furfural and 5-hydroxymethylfurural over carbon-supported PtCo nanocrystals, Gorte and co-workers reported that a surface cobalt oxide layer weakens the interaction of the furan ring with the surface which helps prevent over-hydrogenation and ring opening [38, 130], an effect that is similar to what we have observed for Zn. In contrast, Do et al. have studied the HDO of m-cresol over alumina-supported Pt and PtCo catalysts and reported that the addition of Co increases the overall HDO activity and the rate of formation of the saturated ring product, methylcyclohexane [132]. These previous studies have motivated us to expand our studies of oxyphilic metal modifiers on the HDO activity of Pt to include Co. In particular, in the
work reported here we have investigated the adsorption and reaction of anisole on Pt(111) surfaces modified with Co adatoms with the goal of elucidating how the Co modifier affects the interaction of the aromatic ring with the surface and the overall reaction pathways.

7.2 Experimental

In this study temperature programmed desorption (TPD) was used to assess surface reaction pathways and high resolution electron energy loss spectroscopy (HREELS) was used to identify adsorbed reaction intermediates and their bonding configurations. These experiments were conducting using an ultra-high vacuum (UHV) surface analysis system that had a base operating pressure of $2 \times 10^{-10}$ Torr and was equipped with a quadrupole mass spectrometer (SRS RGA200), an ion sputter gun (PHI electronics), optics for low energy electron diffraction (LEED, OCI), and an HREEL spectrometer (LK Technologies). A Pt(111) single crystal that was 10 mm in diameter was used as a model catalyst. The Pt(111) sample was spot-welded to two tantalum wires that connected to a UHV sample manipulator which allowed it to be heated resistively and cooled to 110 K by conduction from a liquid N\textsubscript{2} reservoir. Prior to reactivity studies a clean and well-ordered Pt(111) surface was prepared by repeated cycles of 2 kV Ar\textsuperscript{+} ion bombardment at 600 K for 40 min, followed with annealing at 1200 K in $2 \times 10^{-8}$ Torr O\textsubscript{2} and vacuum for 10 min respectively. Typically, 6 to 8 cycles of this procedure were needed to achieve a clean Pt(111) surface.

Model PtCo bimetallic catalysts were prepared by vapor depositing Co atoms onto the Pt(111) surface using an evaporative Co source that that consisted of a small coil of Co wire (Alfa Aesa, 99.995%) wrapped around a resistively-heated tungsten filament. The Co
flux from the source was monitored using a quartz crystal microbalance (QCM) located midway between the metal source and the sample, but positioned below the sample to avoid blocking of the flux of atoms to the Pt crystal. The interaction of Co atoms with a Pt(111) surface and the thermal stability of Co-modified Pt(111) surfaces has been previously studied by Chen and co-workers [133, 134]. In these studies it was shown that vapor-deposited Co atoms remain on top of the Pt(111) surface for temperatures below 700 K, while at higher temperatures they diffuse into the bulk. Since the goal of the present study was to assess how Co-addition to Pt affects reactivity through both electronic effects and by providing specific binding sites, we chose to use a Pt(111) surface that was decorated with Co adatoms as a model PtCo alloy surface. Such surfaces were easier to reproducibly prepare and control the number of exposed Co and Pt atoms compared to surfaces in which a portion of the Co was allowed to go sub-surface. A freshly prepared surface was used for each TPD run and HREELS temperature series.

The reactant, anisole (Sigma Aldrich, 99.7%), was contained in a glass vial attached to a stainless-steel manifold that was connected to the main UHV apparatus via a variable leak valve. A 0.6 L dose of anisole was used in both the TPD and HREEL experiments. This dosage was found to correspond to slightly greater than saturation coverage of anisole. A 3 K/s heating rate was used for each TPD run, and the HREEL spectra were collected using a 4 eV electron beam oriented at 60° with respect to the surface normal. The resolution of each HREEL spectrum as determined by the full-width at half-maximum of the elastic peak was ~40 cm⁻¹.
7.3 Results and Discussion

7.3.1 Anisole reaction on Pt(111)

To provide base case data we initially used TPD to investigate the adsorption and reaction anisole on Pt(111). Figure 7.1 displays TPD data obtained from Pt(111) following 0.6 L exposure of anisole. The spectra contain a low-temperature anisole peak centered at 235 K which corresponds to the desorption of physisorbed anisole, and a broad anisole peak centered at 375 K which corresponds to chemisorbed anisole molecules. Benzene was observed in a broad peak between 300 and 550 K, with the peak center near 430 K. Other than benzene, the only reaction products detected were CO and H₂. The H₂ was produced in two distinct peaks centered at 360 and 490 K, with a much broader feature spanning from 540 to 750 K. CO desorbed in two peaks centered at 430 and 490 K. With the exception that benzene was observed, these data are in agreement with that reported in our previous study [123]. These results are also similar to those reported previously by Réocreux et al. [135] who also observed benzene as a product, although they reported only a single CO peak centered at 440 K. This difference may be related to the different anisole doses used in the two studies.
Figure 7.1: TPD spectra obtained following exposure of the Pt(111) surface to 0.6 L of anisole.

In our previous study [123] we concluded based on HREELS data that anisole undergoes O-CH₃ bond cleavage on Pt(111) at temperatures as low as 250 K to form an oxocyclohexadienyl-structured intermediate (C₆H₆O) that bonds to the surface in an η⁵-π configuration. While the reader is referred to this previous study for a detailed analysis of the HREELS data that led to this conclusion, the most salient aspects of the analysis can be gleaned from the data in Figure 7.2, which includes HREEL spectra for anisole-dosed Pt(111) at 115 K and 300 K. The spectrum at 115 K is consistent with that expected for molecular anisole (see peak assignments in Table 7.1). Heating to 300 K, however, results in significant changes in the spectrum of the adsorbed species including, most notably, the emergence of a peak at 1630 cm⁻¹ which is characteristic of a ν(C=O) mode, the disappearance of the intense peak at 780 cm⁻¹ which corresponds to the aromatic ring breathing mode of the intact anisole molecule, and a significant decrease in the
intensity of the ν(C-H) mode at 3000 cm⁻¹ which corresponds to the C-H stretching mode of the aromatic ring. All of these changes are consistent with cleavage of the O-CH₃ bond to form the oxocyclohexadienyl intermediate. Ihm and White have previously reported that phenol also reacts on Pt(111) to form the same oxocyclohexadienyl intermediate [111]. For comparison, we have included in Figure 7.2 an HREEL spectrum obtained in our laboratory for phenol-dosed Pt(111) heated to 300 K. The similarities between this spectrum and that of the anisole-dosed Pt(111) at 300 K are striking. Recently, based on DFT computational results Rérocreux et al. [135] also proposed that anisole reacts on Pt(111) to form a similarly-structured phenoxy-like intermediate that bonds to the surface via the aromatic ring. Together these results further confirm our assignment of the spectrum of the anisole-dosed surface to an oxocyclohexadienyl intermediate.

Figure 7.2: HREEL spectra of oxocyclohexadienyl intermediate on Pt(111) and Co/Pt surfaces formed from anisole and phenol.
Table 7.1: vibrational mode assignment of anisole on Pt(111) and Co/Pt(111) surfaces.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm(^{-1}))</th>
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<tbody>
<tr>
<td></td>
<td>IR/Raman [104-106]</td>
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<tr>
<td></td>
<td>Pt(111) [123]</td>
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<td></td>
<td>Zn/Pt(111) [123]</td>
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<td></td>
<td>Co/Pt(111)</td>
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<tr>
<td>(\gamma(C-C))(_{\text{ring}}) (out of plane mode)</td>
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<tr>
<td></td>
<td>500</td>
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<td></td>
<td>500</td>
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<td>(\gamma(C-H))(_{\text{ring}}) (out of plane mode)</td>
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<tr>
<td>(\gamma(C-H))(_{\text{ring}}) (out of plane mode)</td>
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<tr>
<td>(\delta(C-H))(_{\text{ring}}) (in plane mode)</td>
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<td>1010</td>
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<tr>
<td>(\delta(C-C))(<em>{\text{ring}}) (in plane mode) + (\delta(C-H))(</em>{\text{methyl}})</td>
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<td>(v(C=O))</td>
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<td>(v(C-H))(_{\text{methyl}})</td>
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<td>(v(O-H))</td>
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<tr>
<td>(v(Zn-O))</td>
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<td>400</td>
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<tr>
<td>(v(Pt-C))</td>
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<td>470</td>
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<td>460</td>
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s – symmetric, as – asymmetric, b – bend, v – stretch, \(\delta\) – deformation, \(\rho\) – rock, \(\gamma\) – wag, \(\chi\) – scissor

Our TPD and HREELS results show that the majority of the adsorbed oxocyclohexadienyl species derived from anisole undergo unselective decomposition to produce CO, H\(_2\), and adsorbed hydrocarbon fragments; however, as noted above, some benzene is produced during TPD in a broad peak between 300 and 550 K. It is noteworthy that a significant amount of CO is also produced in this temperature range (Figure 7.1). Based on their DFT calculations, Récureux et al. [135] have proposed that the benzene producing pathway proceeds through an oxocyclohexadienyl species with cleavage of the Ph-O bond being facilitated by adsorbed methyldene or C atoms which were formed as byproducts from the initial O-CH\(_3\) bond cleavage as shown in Figure 7.3. This pathway could therefore also be responsible for the low-temperature CO product observed in Figure 7.1.
7.3.2 Anisole reaction on Co/Pt(111)

Similar to our previous studies of Zn-decorated Pt(111) surfaces [80, 100, 129], the addition of Co adatoms to the Pt(111) surface significantly altered the activity of the surface for the reaction of anisole. This is illustrated by the TPD data in Figure 7.4, which was obtained from 0.4 ML Co/Pt(111) surface dosed with 0.6 L of anisole at 115 K. Consistent with the Co-free surface, anisole was observed to desorb in a narrow peak at 240 K and a somewhat smaller and broader peak 370 K which can be attributed to physisorbed anisole, and chemisorbed anisole molecules, respectively. Hydrogen and carbon monoxide were the only other products observed with H₂ desorbing in two distinct peaks centered at 390 and 540 K, and a much broader peak from 600 to 770 K, and CO desorbing primarily in a peak centered at 430 K, with several minor peaks spanning from 500 to 800 K. Benzene was not observed as a product from the Co/Pt(111) surface.
To provide insight into the reaction pathways for anisole on 0.4 ML Co/Pt(111) and identify stable surface intermediates and their binding configurations, HREELS data for a 0.4 ML Co/Pt(111) surface dosed with 0.6 L of anisole were collected as a function of the surface temperature. These data are displayed in Figure 7.5. Note that for each spectrum, the sample was heated to the indicated temperature and then rapidly quenched to 115 K, at which point the spectrum was collected. The spectra obtained at 145 and 200 K, which are below the desorption temperature of the physisorbed anisole, are consistent with that expected for molecular anisole. Individual peak assignments along with a comparison to those in the IR and Raman spectra of anisole [104-106] and the HREELS spectrum of molecular anisole on Pt(111), as reported in our previous study [123], are given in Table 7.1.
Figure 7.5: HREEL spectrum as a function of temperature for Co/Pt(111) dosed with 0.6 L anisole at 115K.
Heating the surface to 250 K and then 350 K led to significant changes to the HREEL spectra. These include a large decrease in the intensity of the ring breathing mode at 750 cm\(^{-1}\) and an increase in the intensity of a peak at 840 cm\(^{-1}\) which has become the dominant peak between 500 and 1000 cm\(^{-1}\). Peaks also emerged at 1630, 1800, and 2050 cm\(^{-1}\), with the latter two corresponding to the \(\nu(C-O)\) mode of CO adsorbed in Pt bridging and atop sites, respectively. Changes are also apparent in the C-H stretching region where the intensity of the \(\nu(C-H)_{\text{methyl}}\) peak (2880 cm\(^{-1}\)) increased relative to that of the \(\nu(C-H)_{\text{ring}}\) peak (3000 cm\(^{-1}\)). The appearance of the bridging and atop CO species indicates that unselective decomposition of some of the adsorbed anisole commences around 300 K. The other changes in the spectrum, including the emergence of a \(\nu(C=O)\) peak at 1630 cm\(^{-1}\), however, are comparable to those discussed above for the reaction of anisole on Pt(111) to form the oxocyclohexadienyl species. Indeed as shown in Figure 7.2, the HREEL spectra for anisole-dosed Pt(111) and Co/Pt(111) after heating to 300 K are similar indicating that the oxocyclohexadienyl species is also formed on the Co/Pt(111) surface.

While the two spectra clearly correspond to the same intermediate, it is noteworthy that the intensity of the \(\nu(C=O)\) peak at 1630 cm\(^{-1}\) is somewhat less in the spectrum from Co/Pt(111) compared to that from clean Pt (see Figure 7.2). This change in peak intensity can be attributed to a difference in the bonding geometry for the oxocyclohexadienyl intermediate on the two surfaces. On Pt(111) bonding via the \(\pi\) electrons in the ring results in the C=O bond being tilted away from the surface as shown in Figure 7.3[111, 123, 135]. The decrease in the intensity of the \(\nu(C=O)\) peak for this intermediate on the Co/Pt(111) surface indicates that the C=O bond is now oriented more parallel to the surface. Such an orientation would result in a stronger induced image dipole.
in the surface which would decrease the cross-section for exciting this mode. We postulate that this change in bonding configuration is a result of the oxygen in the carbonyl group interacting with an oxyphilic Co adatom on the Pt(111) surface as shown in Figure 7.6. This conclusion is consistent with what we have observed previously for Pt(111) surfaces modified with oxyphilic Zn adatoms [95, 123] where the oxygens in both alcohols and carbonyl compounds preferentially bond to the Zn sites on these surfaces.

The heating of the anisole-dosed Co/Pt(111) surface to 450 K produced additional changes in HREEL spectrum of the adsorbed intermediates, including the disappearance of the ν(C=O) peak at 1630 cm⁻¹, a large decrease in the intensity of the peaks between 1000 and 1500 cm⁻¹, an increase in the intensity of the ν(C-Pt) peak at 460 cm⁻¹, and an increase in the intensity of the ν(C-O) peaks at 1800 and 2050 cm⁻¹. While these changes may be partially due to some unselective decomposition of the oxocyclohexadienyl intermediate, the persistence of the intense peak at 840 cm⁻¹ which is at an energy characteristic of the out-of-plane bending modes of an aromatic ring (see Table 7.1) suggests that the ring structure remains intact. This observation along with the disappearance of the ν(C=O) peak suggests that cleavage of the C-O bond in the oxocyclohexadienyl intermediate has

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**Figure 7.6**: Proposed reaction pathway for adsorption and reaction of anisole on Co/Pt(111) surface.
occurred, resulting in the formation of adsorbed benzene or phenyl groups, as shown in Figure 7.6.

![HREEL spectra of benzene intermediate on Co/Pt(111) surface formed from anisole or benzene](image)

To help verify this hypothesis, we compare the HREEL spectrum of the anisole-dosed Co/Pt(111) surface heated to 400 K with the HREEL spectrum of benzene on Co/Pt(111) at 300 K in Figure 7.7. Except for the different intensities of the \( \nu(\text{C-O}) \) peaks at 1800 and 2050 cm\(^{-1}\) (the small C-O stretching peaks in the spectrum of the benzene-dosed sample are a result of CO adsorption from the background gas in the UHV chamber), the two spectra are quite similar. As discussed in the literature [136] the peaks at 1150 and 1440 cm\(^{-1}\) can be assigned to in-plane C-H and C-C modes. Since benzene adsorbs on Pt(111) with the aromatic ring parallel to the surface [136], these modes are oriented parallel to the surface which, due to the induced image dipole in the metal, have low excitation cross-sections. The similarity of these two spectra, therefore, provides support for the conclusion that on Co/Pt(111) the oxocyclohexadienyl intermediate undergoes C-O bond cleavage.
near 400 K to produce adsorbed benzene with the hydrogen required for this reaction being supplied by the unselective decomposition pathway. The adsorbed oxygen produced by this reaction appears to react with surface carbon which could also be produced by the unselective decomposition pathway to produce the CO that was observed at 430 K in the TPD experiment (Figure 7.4).

Based on this analysis we propose the pathway depicted in Figure 7.6 for the selective HDO of anisole on Co/Pt(111) to produce CO, H₂ and adsorbed benzene. This pathway is similar to that proposed by Réocreux et al. [135] for the reaction of anisole on Pt(111) (see Figure 7.3) with the Co acting as the oxyphilic site that interacts with the oxygen rather than an adsorbed C atom. We suspect that Co would be more effective in this role than C, but it is not possible to make this determination using the data obtained in the current study. It is also not clear why in the case of Pt(111) some of the benzene HDO product desorbs intact while for Co/Pt(111) it remains on the surface and decomposes at higher temperatures.

As noted in the introduction, our previous studies of the reaction of lignin-derived molecules on Zn-modified Pt(111) surfaces motivated the present study of the reaction of anisole on Co/Pt(111) with the goal of providing further insight into how oxyphilic modifiers on Pt influence the selectivity for HDO reactions [100, 123, 129]. Comparing the results obtained in the present study with those from our previous studies of Zn/Pt(111) reveals that the Zn and Co modifiers have some similarities, but there are also some significant differences. In both cases, the oxyphilic metals interact with the oxygen atoms in alkoxide groups in aromatic oxygenates, such as anisole, which helps facilitate C-O bond cleavage. The reaction pathways for anisole on Zn/Pt(111), however, are substantially
different from those observed here for Co/Pt(111). In our previous studies we showed that, in addition to providing an adsorption site for the oxygen functionalities, Zn also has a strong electronic effect which destabilizes the bonding of aromatic rings with the Pt(111) surface [80, 100, 123, 129]. This destabilization is sufficient to change the most stable bonding configuration for anisole from one where the aromatic ring is situated parallel to the surface to one where the ring is tilted away from the surface. Indeed, on Zn/Pt(111), anisole adsorption occurs exclusively via interaction of the -O-CH$_3$ oxygen with a surface Zn site, with the aromatic ring tilted away from the surface. In the context of HDO catalysis, this is a desirable characteristic of the Zn modifier since it helps limit ring hydrogenation and enhances the selectivity for the production of the desired aromatic hydrocarbons as we have demonstrated in reactor studies with high surface area PtZn/C catalysts [123]. In contrast, the reaction of anisole on Co/Pt(111) is similar to that on the unmodified Pt(111) surface with the ring interacting strongly with the surface and cleavage of the O-CH$_3$ bond resulting in the formation of an oxocyclohexadienyl intermediate. This species then undergoes Ph-O bond cleavage which is mediated by Co or C sites on the Pt surface to produce benzene or an adsorbed phenyl group. Since Co addition does not destabilize the interaction of the ring with the Pt surface, PtCo catalysts are likely to promote both C-O bond hydrogenolysis and ring hydrogenation. A study by Do et al. on the HDO of $m$-cresol over PtCo/γ-Al$_2$O$_3$ which showed a high selectivity to methylcyclohexane supports this conclusion [132].
7.4 Conclusions

The results obtained in this study provide insight into the reaction of anisole on Pt(111) and Co-modified Pt(111) surfaces. On both surfaces, anisole undergoes O-CH₃ bond cleavage at relatively low temperatures to form an oxocyclohexadienyl-structured intermediate that bonds to the surface in a η⁵-π configuration. Subsequent to this reaction, interaction of the O atom in oxocyclohexadienyl with oxyphilic Co and/or C sites on the Pt surface facilitates Ph-O cleavage to form adsorbed benzene or phenyl groups. In parallel with this reaction pathway unselective decomposition to produce adsorbed CO, H, and hydrocarbon fragments also occurs.

Comparing the results obtained here for Co-modified Pt(111) with those reported previously for Zn-modified Pt(111) reveals the both the Zn and Co atoms provide bonding sites for the oxygen in the alkoxide group in anisole which helps facilitate selective C-O bond cleavage. Zn was also found to have a strong electronic effect that destabilizes the interaction of aromatic rings with the Pt(111) surface, while a similar effect was not observed for Co.
Chapter 8 Conclusion

This project has focused on understanding the catalytic mechanism of HDO upgrading on bimetallic catalytic surface for biomass-derived oxygenates, especially the lignin fraction. With the help of surface science techniques such as TPD and HREELS, it has been demonstrated that the addition of a more oxyphilic metal can greatly enhance the desired HDO activity and selectivity compared with group 10 metal only catalyst. Chapter 3 identifies the reaction of furfural on Pt(111) and Zn/Pt(111) surface. It is determined that furfural molecule interacts with Pt(111) surface via a parallel geometry, which facilitates ring opening at low temperature (~200 K). In contrast, a $\eta^2$(C, O) configuration is formed on the Zn/Pt(111) surface with the aromatic ring tilted away from the surface. Such binding configuration weakens the carbonyl C-O bond, consequently facilitates its cleavage. Meanwhile, the aromatic nature can be greatly preserved as the ring is kept away from the surface. This study suggests the Zn addition alters the reaction of furfural on Pt(111) surface in the following two aspects, (1) providing a specific binding site for oxygen and therefore facilitating selective C-O bond cleavage, (2) limiting the interaction between aromatic ring and the catalytic surface via electronic effect.

The effectiveness in facilitating HDO reaction of furfural suggests PtZn may be effective in the upgrading of lignin-derived oxygenates. Benzaldehyde is then picked as a model molecule, and its reaction on Pt(111) and Zn/Pt(111) surface is described in Chapter 4. Since most HDO reaction is conducted under a high hydrogen pressure environment, benzaldehyde reaction was studied on the catalytic surfaces pre-dosed with H$_2$. Similar to the furfural study, benzaldehyde was found to interact strongly with the P(111) surface via the phenyl ring, while a $\eta^2$(C, O) configuration formed on the Zn/Pt(111) surface with the
phenyl ring tilted up. Consequently, total decomposition of benzaldehyde was observed on the Pt(111) surface as low as 350 K, while HDO product toluene was produced on the Zn/Pt(111) surface.

Except for the aldehyde functional group, the Ph-O-C linkage is also commonly found in lignin-derived oxygenates. Anisole is therefore selected as the next model molecule, and the reaction is studied under both UHV chamber and liquid phase flow reactor as described in Chapter 5. Anisole was found to bond to the Zn/Pt(111) surface via the oxygen lone pair electron on Zn adatom, with the aromatic ring tilted away from the surface in the UHV chamber. Such binding configuration facilitated selective C-O bond cleavage and kept the aromatic ring intact. On the other hand, parallel geometry and strong interaction between the aromatic ring and Pt(111) surface was observed, which facilitated ring saturation and unselective decomposition. Comparing with the UHV study, consistent results were observed from the flow reactor: ring saturation products was observed with high selectivity on the Pt only catalyst, while, selective C-O bond cleavage and limited ring hydrogenation was observed for the PtZn catalyst.

Since biomass-derived oxygenates usually contain multiple functional groups, study of guaiacol reaction on Zn/Pt was described in Chapter 6 as an expansion of our previous study described in Chapter 4 and Chapter 5. For Zn-free Pt(111), guaiacol interacted with the surface via the π-orbitals of the aromatic ring, making the ring situated parallel to the surface. Such binding configuration promoted unselective decomposition at low temperatures. On the other hand, Zn addition on Pt(111) surface provided a specific binding site for the oxygen atoms in the guaiacol molecules, which later facilitated selective -O-CH₃ bond cleavage. Meanwhile, the binding configuration was also greatly altered, the
aromatic ring interacted with the catalytic surface less strongly and titled away from the surface, limiting the possible ring saturation under typical HDO reaction condition.

While the studies described in Chapter 3 to Chapter 6 provided considerable insight into how Zn alters the HDO activity of Pt, it is not clear how general these observations are and if the addition of other oxyphilic metals to Pt will have a similar effect. Cobalt is an oxyphilic metal that has been used to modify the HDO activity of Pt and the reaction of anisole on Co/Pt(111) was then studied and described in Chapter 7. On both Pt(111) and Co/Pt(111) surfaces, same reaction intermediate oxocyclohexadienyl was formed and bond to the surface similarly, via a $\eta^5$-$\pi$ configuration. Two following reaction pathways were observed on the Pt(111) surface from such intermediate: part of the oxocyclohexadienyl decomposed to CO, H$_2$ and hydrocarbon fragments directly, and the rest reacted with the C on surface to produce benzene and CO. In contrast, selective Ph-O bond cleavage of the oxocyclohexadienyl intermediate was observed on the Co/Pt(111) surface, facilitated by the Co adatoms. Comparing the role of Zn modifiers described in Chapter 3 to Chapter 6, both Zn and Co were observed to interact strongly with the oxygen in the alkoxide or aldehyde functional groups and help to facilitate C-O bond cleavage. However, the electronic effect brought by the Co addition differs dramatically from the Zn addition. When a parallel geometry between the ring and catalytic surface was observed on the Co/Pt(111) surface, much weaker interaction observed on Zn/Pt(111) with the ring tilted away from the surface.
Reference


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