Selective Hydrodeoxygenation Of Biomass-Derived Model Compounds Over Bifunctional Catalysts

Tianqi Chen
University of Pennsylvania

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Selective Hydrodeoxygenation Of Biomass-Derived Model Compounds Over Bifunctional Catalysts

Abstract
The negative social and environmental impacts from burning of fossil fuels motivated the development of renewable and sustainable sources for the production of electricity such as wind and solar. Lignocellulosic biomass has emerged as a promising feedstock for carbon-based fuels and chemicals and much research effort has recently been directed at developing efficient catalytic pathways for the upgrading of lignin-derived oxygenate into useful products. This dissertation aimed to study the viability of utilizing bifunctional catalysts consisting of a transition metal either supported on or modified by a reducible metal oxide to promote the direct C-O bond cleavage in aromatic oxygenates (m-cresol). Surface science techniques such as HREELS, XPS and TPD were used to provide insights into the reaction pathway and mechanism of this reaction. In all studies featured in this thesis, transition metals such as Pt and Ni, exhibit moderate selectivity to desired product, toluene. It was found that the strong interaction between aromatic rings and metal surfaces facilitates the ring hydrogenation which forms an intermediate pool. While metal catalysts promoted by WOx and NbOx are extremely active and selective for the direct deoxygenation reaction. The interaction at the metal-metal oxide interfaces helps keep the metal oxide partially reduced and provide the active bonding sites for the adsorption of hydroxyl groups. It was also found that the m-cresol tends to adsorb on oxygen vacancies while the aromatic rings are tilted away from the surface. This bonding configuration would promote the direct deoxygenation of hydroxyl group.

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SELECTIVE HYDRODEOXYGENATION OF BIOMASS-DERIVED MODEL COMPOUNDS OVER BIFUNCTIONAL CATALYSTS

Tianqi Chen

A DISSERTATION

in

Chemical and Biomolecular Engineering

Presented to the Faculties of the University of Pennsylvania

in

Partial Fulfillment of the Requirements for the

Degree of Doctor of Philosophy

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ABSTRACT

SELECTIVE HYDROGENATION OF BIOMASS-DERIVED MODEL COMPOUNDS OVER BIFUNCTIONAL CATALYSTS

Tianqi Chen

John M. Vohs

The negative social and environmental impacts from burning of fossil fuels motivated the development of renewable and sustainable sources for the production of electricity such as wind and solar. Lignocellulosic biomass has emerged as a promising feedstock for carbon-based fuels and chemicals and much research effort has recently been directed at developing efficient catalytic pathways for the upgrading of lignin-derived oxygenate into useful products. This dissertation aimed to study the viability of utilizing bifunctional catalysts consisting of a transition metal either supported on or modified by a reducible metal oxide to promote the direct C-O bond cleavage in aromatic oxygenates (m-cresol). Surface science techniques such as HREELS, XPS and TPD were used to provide insights into the reaction pathway and mechanism of this reaction. In all studies featured in this thesis, transition metals such as Pt and Ni, exhibit moderate selectivity to desired product, toluene. It was found that the strong interaction between aromatic rings and metal surfaces facilitates the ring hydrogenation which forms an intermediate pool. While metal catalysts promoted by WO_x and NbO_x are extremely active and selective for the direct deoxygenation reaction. The interaction at the metal-metal oxide interfaces helps keep the metal oxide partially reduced and provide the active bonding sites for the adsorption of
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Chapter 1. Introduction

1.1 Biomass as a Renewable Energy Source

According to Key World Statistics 2018 [1], the fast consumption of fossil fuels (11600 Mtoe) accounting for 81% of the world’s primary energy consumptions brought a range of negative social and environmental impacts, like energy crisis, climate changes and air pollutions, and motivated the development of renewable and clean energy sources. Biomass, which includes plant biomass and animal biomass, is considered as an attracting feedstock for fuels and chemicals. Generally, plants converted the energy from sun into chemical energy by the process of photosynthesis. Those chemical energy were ‘fixed’ or stored in the form of terrestrial and aquatic vegetation. The vegetation when grazed by animals get converted into animal biomass. In the past, biomass was used to combust the wood and corps directly which had low efficiency and emitted more CO₂ than coal combustion [2,3].

Modern biomass upgrading, including biochemical and/or thermochemical processes [4], makes biomass the second largest energy source which is equivalent to other renewable energy sources, like solar, wind and heat. During biochemical processes, biomass is converted to biofuels through the digestive action of living organisms while it is converted to biofuels, chemicals and gases by applying heat and/or pressure in the thermochemical processes. Compared to other renewable energy sources such as solar and wind, biomass has few problems with energy storage. The renewability and substantiality of biomass provides a potential solution to the global energy crisis and a promising way to address problems arising from burning of fossil fuels.
The need to replace the diminishing fossil fuels with a renewable and sustainable feedstock prompted the research to develop catalytic pathways to effectively upgrade the biomass into useful liquid hydrocarbon fuels and chemicals. The work in this thesis mainly focused on addressing this need for a specific fraction of biomass, lignocellulosic biomass.

1.2 Primary Upgrades of Lignocellulosic Biomass

Lignocellulosic biomass, mainly from agriculture, forest and industrial wastes, is composed of three organic constituents: cellulose, hemicellulose and lignin. The compositions of these three components depends on the type of biomass and part of the plant sampled. As shown in Figure 1.1, cellulose, the largest single component of lignocellulosic biomass, is a linear polysaccharide, typically consisting of thousands of D-glucose monomers. The intra- and intermolecular interactions between hydrogen bonds from hydroxyl groups in each monomer make cellulose a crystalline structure. Hemicellulose is a polysaccharide composed of various carbohydrate monomers, mainly xylose, arabinose, mannose. It has much lower degree of polymerization than cellulose, around 50-200 monomers. Amorphous structure of hemicellulose with little strength makes it less stable and easily hydrolyzed by dilute acid or base as well as hemicellulose enzymes. Lignin comprises 15-30% of the biomass weight and is rich in aromatic functionality and consists of linked phenylpropane units making it more difficult to decompose.
Figure 1.1 Structure of lignocellulosic biomass with cellulose, hemicellulose, and lignin represented (from [5]).

Lignin contains approximately 40% of the possible energy of the biomass due to its high C/H ratio and this has prompted research on its upgrading. Gasification is one scheme for doing this as shown in Figure 1.2. Under high temperature treatments, gasification of lignocellulosic biomass with stream and/or oxygen produces synthesis gas containing mainly H₂, CO and CH₄ [5–7]. The composition of the produced gas is influenced to a large content by the gasification technology, i.e., by the type of reactor, the gasification agent, and the operating conditions. Syngas can be further upgraded into fuels and chemicals by reactions such as water gas shift, steam reforming and Fischer-Tropsch synthesis. However, the gasification process is energy intensive, and it cannot make use of the valuable chemical structures and functional groups that are present in the original biomass.
Pyrolysis is another approach for breaking down biomass and consists of the thermal decomposition of materials in the absence of oxygen or when significantly less oxygen is present than required for complete combustion. As the most efficient process for biomass conversion and the most promising energy sources, it is considered as an alternative to eventually replace non-renewable fossil fuels. Based on the operating conditions, the pyrolysis process can be divided into three subclasses: conventional pyrolysis, fast pyrolysis and flash pyrolysis. Conventional pyrolysis has been used to produce charcoal with relatively slow heating rates for thousands of years while fast pyrolysis is a process in which biomass is rapidly heated to high temperatures in the absence of oxygen. The latter produces 60-75 wt.% of liquid bio-oil, 15-25 wt.% of solid char, and 10-20 wt.% of noncondensable gases [9]. There are four features for fast pyrolysis. First, high heating and heat transfer rate are used. Second, the reaction temperature is carefully controlled between 698 K and 773 K. Third, short vapor residence times are used.
(typically < 2s). Fourth, pyrolysis vapors and aerosols are rapidly cooled to bio-oil which consists of water and more than 300 organic components such as alcohols, phenols, aldehydes and organic acids which are difficult to separate.

The third processing techniques, liquid-phase processing is a more complex and selective process including multiple steps to produce high value chemicals or fuels. The lignocellulosic biomass is deconstructed by thermal, and/or chemical/catalytic methods to produce functional intermediates. Before the chemical/catalytic method, usually a pretreatment step involving removal of the hemicellulose stream and lignin is used [10,11]. Then the hemicellulose stream and lignin can be upgraded using bimetallic catalysts to a range of end products like furfural, glucose, 5-hydroxymethylfurfural (HMF) [12,13].

The lignin component in biomass is rich in aromatic functionality and more stable than cellulose and is an attractive feedstock for production of useful aromatic chemicals. However, oxygen-linked phenylpropane units makes it difficult to break down into smaller molecules. Fast pyrolysis of lignin has been demonstrated and produces highly polar aromatic species such as those shown in Table 1.1, which have a range of oxygen-containing functional groups such as aldehyde, hydroxyl, ketone, which are unstable and immiscible in hydrocarbons [14,15]. Thus, the removal of some of the oxygen functionalities in these molecules is an important step in lignocellulosic biomass upgrading. This need has motivated the studies described in this thesis which focus on developing catalytic pathways and catalysts that are active and selective for the hydrogenolysis of C−O bonds in oxygenated aromatics that produced by the pyrolysis of the lignin fraction of
biomass. The results of this study have led to the development of various kinds of catalysts including supported noble metals, bimetallic, and bifunctional catalysts that improve the efficiency and selectivity of hydrodeoxygenation. More details will be discussed below.

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Table 1.1 Pyrolysis products from lignin (adapted from [14]).
1.3 Catalysts and Reaction Pathways for Upgrading Lignin Pyrolysis Products

The need to partially or completely remove oxygen functionalities and yield high-value aromatic products from lignin-derived molecules has prompted research into the development of highly active and selective catalysts for hydrodeoxygenation (HDO) of aromatic oxygenates. Early studies in this area focused on using industrial hydrotreating catalysts such as Co-MoS$_2$ and Ni-MoS$_2$ which were used to remove sulfur, nitrogen and oxygen from petrochemical feedstocks. Among MoS$_2$-based catalysts, Co and Ni donate electrons to the active sites (Molybdenum) which weakens the bonding between molybdenum and sulfide, thereby generating the active sulfur vacancy sites for HDO reaction [16–19]. For example, V.N Bui et al. [18] found that Co-MoS$_2$ effectively catalyzes the reaction of guaiacol to benzene by a direct deoxygenation pathway.

Other early studies focused on noble metals on acid/base supports such as Pt/$\gamma$-Al$_2$O$_3$ and Pd/SiO$_2$. These catalysts typically show a better activity and selectivity for HDO reaction than MoS$_2$-based catalysts [20–23]. Using $m$-cresol as a representative lignin derived molecule, it has been proposed that the HDO reaction on noble metals involves the initial hydrogenation of the aromatic ring to produce a tautomerization pair, followed by hydrogenation, dehydrogenation and/or dehydration to remove the oxygen-containing functional groups, as shown in Figure 1.3(a). Brönsted acid sites on the oxide support were proposed to activate the C-O bonds. In the meantime, noble metals dissociate H$_2$ and provide the atomic hydrogen for the reaction. However, oxides support such as alumina can strongly bind the oxygenates like phenols which block the active sites and result in
coking [16,24,25]. Considering the moderate performance and price of supported noble metal catalysts, less expensive base metals such as Ni, Co and Fe were also studied [26–28]. For example, Fe/SiO₂ was found to be selective to convert guaiacol to benzene and toluene over a range of temperatures [26]. Co turned out to be more active than Fe but was found to promote the decomposition of the aromatic hydrocarbons [26]. Although they exhibit high HDO ability without ring opening and ring saturation products, activity was lower than the noble metals.

![Proposed pathways for HDO of aromatic oxygenate over various catalysts.](image)

**Figure 1.3** Proposed pathways for HDO of aromatic oxygenate over various catalysts.

What’s more, transition metal phosphides and carbides have also been explored for HDO reactions. Mechanism of deoxygenation over phosphides was hypothesized to depend on the presence of both metallic and acidic groups. For example, for the reaction of anisole on supported Ni₂P catalyst [29], the demethylation of anisole to form phenol is followed by hydrogenolysis and hydrogenation. P-OH groups could provide Brönsted acid
sites while Ni maintains the metallic behavior. Ni$_2$P catalyst was found to have two crystal structures. One is that a tetrahedral geometry of Ni sites and 4 neighboring P atoms are active for decarbonylation. The other one is that Ni sites with 5 P neighbors in a pyramidal geometry can promote the HDO [30–32]. By increasing the number of the latter configuration, it would facilitate the HDO activity and decrease the decarbonylation rate. For carbides, the binding of the metal to carbon atoms shifts the energy of the transition metal d electrons to lower energies [32–34]. For example, WC shows ability to activate the C-O bonds of propanol and propanal instead of C-C bonds to form propene. The presence of the oxygen on the WC surface introduces acidic sites which are crucial for the dehydration reactions. A similar effect of surface oxygen has been proposed for other carbides like, NiMo and MoC [35–38].

The catalysts mentioned above all suffered severely from the rapid deactivation due to coking and hydrogenation of the aromatic rings which leads to lower-value products. This has prompted the development of bimetallic catalysts by alloying a hydrogenating metal with a second more oxyphilic metal (forms strong metal-oxygen bonds). Many of them are noble-metal-based alloys. A proposed bonding configuration of aromatic oxygenates on bimetallic catalysts is shown in Figure 1.4 [39]. Strong bonds are formed between exophilic metals and oxygen bonds of aromatics, allowing easier C-O scission while the noble metals are used to dissociates hydrogen. As previously studied by our group [40,41], modifying Pt with Zn changes the bonding configuration of aromatic compounds where the primary interaction is via the oxygen with the phenyl ring tilted away from the surface while on unmodified Pt surface, aromatic rings interact strongly with the Pt surface, allowing for the C-C bond scission and ring opening. This bonding configuration would
hinder the hydrogenation of aromatic rings. Meanwhile, Zn provides the active bonding site for selectively C-O cleavage.

Figure 1.4 Hypothesized interaction of aromatic oxygenates with bimetallic catalysts (from [39]).

Besides alloying the noble metals with a second more oxyphilic metal, bifunctional catalysts consisting of a transition metal either supported on or modified by a reducible metal oxide have also been reported to maintain an extremely high selectivity and activity to remove the oxygen-containing functional groups. Examples here include WOₓ-Pt/C [42], Ru/Nb₂O₅-SiO₂ [43], Ru/WOₓ-ZrO₂ [44]. It is, however, not clear why they work so well. We [42,45,46] propose that the interaction at the metal-metal oxide interface helps maintain the metal oxide in a partially reduced state and the resulting oxygen vacancies provide bonding sites for the oxygen atoms in the aromatic oxygenates. This bonding configuration could facilitate the direct scission of the C-O bond as shown in Figure 1.3(b).

The majority of my thesis research has focused on elucidating the mechanism of oxide promotion of noble metal HDO catalysts through the use of model catalysts and surface sensitive spectroscopic probes. The insight obtained in these studies was then used to design highly selective HDO catalysts.
1.4 Surface Science Studies for Biomass Upgrading

Extensive studies on high surface catalysts mentioned above showed that various catalysts exhibit high selectivity and activity for HDO of biomass-derived aromatic oxygenates. However, the traditional reaction studies failed to identify the reaction intermediates and understand the detailed reaction pathway on those catalysts. In an ultra-high vacuum system, surface science techniques like, x-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and high-resolution electron energy loss spectroscopy (HREELS) are used to study the reaction of model compounds on a well-controlled model catalyst. By figuring out the reaction intermediates, molecule bonding configuration and active sites, the mechanism of the reaction, unavailable from reaction studies, can be revealed. To demonstrate the power of the surface science studies, a study on a hydrodeoxygenation of the lignin-derived oxygenate on Pt/Zn bimetallic catalyst by our group is briefly summarized here [41].

The model compound, anisole, with a C-O-C linkage which is commonly found in lignin-derived oxygenates was studied. The Zn/Pt(111) bimetallic catalyst was prepared by depositing Zn on a Pt(111) single crystal by the resistive thermal evaporation method. TPD results on Pt(111) and Zn/Pt(111) catalysts were shown in Figure 1.5. On Zn-free Pt(111) surface, only desorption of H₂ and CO were detected. The desorption peaks at 185 and 215 K result from the physisorbed multiplayers and chemisorbed anisole, respectively. By increasing the temperature to 350 K, the desorption of H₂, which is the characteristic of recombinative desorption of H atom from Pt(111) surface, suggests that the scission of C-H bond from aromatic rings or methyl group of adsorbed anisole has occurred by this temperature. However, on Zn/Pt(111) surface, besides H₂ and CO, a range of products
including CH₄, CH₂O and C₂H₆ were observed (see Figure 1.5(b)). The peak for the recombinative H₂ desorption at 350 K is nearly absent and suggests that anisole is more stable on Zn/Pt(111) surface. The desorption peak of H₂ and CO shifted to higher temperature (> 100 K) and further indicates that anisole-derived species were more stable with the addition of Zn film by decreasing the activity of C-H and C-C bond scission. The emergence of CH₂O peak at 445 K might come from the scission of the Ph-O bond and dehydrogenation.

To better understand the reaction pathway and active sites of the reaction, vibrational spectra of adsorbed intermediates were also collected. HREEL spectra of Pt(111) and Zn/Pt(111) surfaces dosed with 0.6 L of anisole were shown in Figure 1.6. On Pt(111) surface, the intensity of the out-of-plan γ(C-H)ₚₐₑₙ₉ peak at 820 cm⁻¹ increased relative to the in-plane δ(C-H)ₚₐₑₙ₉ peak at 1010 cm⁻¹ suggests that at 200 K, aromatic rings are parallel to the surface in the chemisorbed species. Further heating to 300 K, along with a large decrease in the intensity of the ring breathing mode at 780 cm⁻¹, the decrease of the ν(C-H)ₚₐₑₙ₉ at 3000 cm⁻¹ relative to that of the aliphatic ν(C-H) mode at 2870 cm⁻¹ indicates at least a portion of adsorbed intermediate species started to lose their aromatic feature by this temperature. By heating to 350 K, the emergence of the peaks at 1800 and 2000 cm⁻¹ which results from the adsorption of CO on the atop and bridging sites of Pt(111) indicates the decomposition of the adsorbed intermediates has occurred by this temperature. However, on Zn/Pt(111), at 200 K, the emergence of the in-plane δ(C-H)ₚₐₑₙ₉ mode of anisole at 1000 cm⁻¹ which is absent from the Pt(111) surface is attributed to the different bonding configuration of anisole on Zn-modified surface. It was proposed that the anisole absorbs via the oxygen with the aromatic rings tilted away from surface. By heating to 250
K, the further increase in the intensity of the peak at 1000 cm\(^{-1}\) which is proposed to not only be attributed to the in-plane \(\delta(C-H)\)\text{ring} peak, but also result from the peak of the C-O stretches of alkoxide groups. It indicates that the cleavage of the Ph-O bond in a portion of the adsorbed anisole has occurred by this temperature. Heating the sample to 300 and 350 K, minor changes were observed. The persistence of the characteristic aromatic \(\gamma(C-H)\) peak at 3000 cm\(^{-1}\) suggests that phenyl groups remain intact on the surface compared to the unselectively decomposition of the intermediates on Pt(111) surface.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.5.png}
\caption{TPD data for reaction of anisole on (a) Pt(111) and (b) Zn/Pt(111) surfaces (from [41]).}
\end{figure}
Figure 1.6 HREEL spectra as a function of temperature for (a) Pt(111) and (b) Zn/Pt(111) dosed with anisole at 115 K (from [41]).

The proposed reaction pathways on the Pt(111) and Zn/Pt(111) surfaces are shown in Figure 1.7. On the Pt(111) surface, anisole tends to lay flat on the Pt via the $\pi$-orbitals of the aromatic rings. This bonding configuration would facilitate the hydrogenation of the aromatics rings. While, on Zn-modified Pt(111) surface, the anisole adsorbed through its oxygen on the surface Zn sites or possible an adjacent Pt sites with the phenyl ring tilted away from the surface thereby hindering the hydrogenation of rings.

In these surface science studies, techniques such as TPD and HREELS were very effective in providing insight into reaction pathways and the structure and bonding configuration of reaction intermediates which are difficult to be determined by reaction kinetics studies alone. For example, TPD helped to understand the mechanism of catalytic
reactions including adsorption, surface reaction and desorption. HRRELS reveals the reaction pathway by allowing adsorbed species and their bonding configuration to be determined. In my research, similar approaches were used to understand the how oxide modifiers enhance the HDO activity and selectivity.

Figure 1.7 Proposed pathways and intermediates for the adsorption and reaction of anisole on Pt(111) and Zn/Pt(111) surfaces (from [41]).

1.5 Thesis Objectives

As mentioned in the Section 1.3, various reaction pathways have been proposed for the HDO of the lignin-derived oxygenates. The goal of my thesis is to understand the mechanism and how oxide promoters work in metal-metal oxide catalysts. At the same time, I will use this insight to design and test the high surface area HDO catalysts. The thesis will mainly focus on the following questions regarding the HDO catalysts.

1. How do surface oxide modifiers, such as WOₓ and NbOₓ, enhance the performance of Pt-based catalysts for the HDO of aromatic oxygenates?
2. Are synergistic interactions between the metal and the oxide promoter important and how do they affect the structure or composition of the oxide and its reactivity?
3. Are there any common rules for designing metal-metal oxide bifunctional catalysts that are selective for the HDO of lignin-derived oxygenates?
1.6 Thesis Outline

The first chapter in this dissertation provides the background of my research on designing catalysts for the hydrodeoxygenation of lignin-derived aromatic oxygenates. The prospect and the importance of the biomass as an alternative to fossil fuels are discussed in Section 1.1. The following two sections mention the upgrading process of lignocellulosic biomass and the history of the HDO catalysts respectively. The surface science studies on biomass catalytic upgrading are included in the last section.

Chapter 2 summarizes the experimental methods I have utilized throughout my research. I start by describing the ultra-high vacuum chamber configurations and basic physics of the apparatus used in surface science studies. For experimental designs in reaction studies, first, I mention the design for atmospheric pressure continuous flow reactor. Second, the catalyst synthesis methods are introduced. High surface area catalysts are prepared by incipient-wetness method and the metal oxide film is deposited by atomic layer deposition.

Chapter 3, 4 and 5 demonstrate the HDO reaction of m-cresol model compound on different bifunctional catalysts. Chapter 3 focuses on explaining the extremely high activity and selectivity of the WO\textsubscript{X}-Pt catalyst by understanding the active sites and reaction mechanism. Chapter 4 reveals the potentials for NbO\textsubscript{X}-Pt bifunctional catalyst in facilitating HDO reaction of m-cresol. The interaction at NbO\textsubscript{X}-Pt interface and reaction pathway was also studied. Chapter 5 extends previous study on Pt-based catalyst to WO\textsubscript{X}-modified Ni catalyst. The reactions on both unmodified Ni and WO\textsubscript{X}-Ni catalysts were measured at two temperatures. The conversion and yields as a function of the coverage of
WO$_3$ thin film is also discussed to understand the effect of thickness of the metal oxide thin film.

Finally, Chapter 6 summaries the key finding during my research and concludes the thesis dissertation.
Chapter 2 Experimental

2.1 Introduction

As mentioned in introduction section, the goal of this thesis is to investigate and understand how the surface of a group 10 metal with a metal oxide modifier can enhance the selectivity for the HDO of biomass-derived oxygenates by reaction studies of high surface area catalysts, as well as ultra-high vacuum surface science studies of model catalysts. Firstly, high surface area catalysts were used to give a brief understanding of the reaction kinetics and reaction pathway of catalysts. However, the synergistic effect at metal-metal oxide interface, reaction pathways and active sites of the catalysts are difficult to be interpreted solely by high surface area catalyst studies. To overcome this limitation, surface science techniques, such as Temperature Programmed Desorption (TPD), X-ray Photoelectron Spectroscopy (XPS) and High Resolution Electron Energy Loss Spectroscopy (HREELS), were used to study the HDO of model biomass-derived model compounds on well-defined single-crystal model catalyst surfaces.

2.2 Ultra-high Vacuum Apparatus

2.2.1 Ultra-high Vacuum Chamber Configuration

The surface science studies in this thesis were carried out in two Ultra-high vacuum chambers with $2 \times 10^{-10}$ torr background pressure shown in Figure 2.1. The Ultra-high vacuum chamber was generally consisted with three stages of pumping. In the first stage, a mechanical rotary vane roughing pump (ALCATEL 2008A, not shown in the figure) clears most of the gas from the chamber and pumps the pressure down to around $10^{-4}$ Torr.
This is followed by the second stage a turbomolecular pump (Leybold Turbvac 350iX) which can bring the chamber down to $10^{-9}$ Torr. The ion pump at the bottom of the chamber acts as the third stage of pumping whose optimal operation pressure is around $2 \times 10^{-10}$ Torr. To reach this pressure, the whole chamber needs to be baked out to get rid of the water molecules had adsorbed on the inside chamber wall when chamber was exposed to the air. Basically, several heating tapes were wrapped around the chamber to heat the chamber to approximately 250 °C for over 12 hours. Meantime, a quaternary pump, the titanium sublimation pump was utilized to lower the chamber pressure by the sublimation of the titanium filament which coated the chamber with a thin, reactive film of clean titanium every half an hour. The residual gas, such as H$_2$, in the chamber are likely to react and form a stable, solid product with titanium film.

![Figure 2.1 Schematic of main ultra-high vacuum chamber used during the studies contained herein. The apparatus is shown from the front (a) and back (b).](image-url)
Within the chamber, the configuration of the single crystal sample under study is displayed in Figure 2.2. An electrically insulated, UHV rated, stainless steel feedthrough with both copper power leads and chromel and alumel thermocouple leads supported the sample mounting configuration. The end of the copper power leads was tightly wrapped with a small amount of tantalum foil to allow the spot-welding of tantalum mounting posts. The single crystal was spot-welded to two tantalum mounting posts for conductive cooling and resistive heating purposes. To monitor the sample temperature during heating and cooling, type K (chromel-alumel) thermocouple wires were spot-welded on the back of the crystal and connected to their corresponding feedthrough leads. A power supply connected with copper power leads can pass 0-10 amps of current to single crystal thereby heating it up to 1200 K. Conductive cooling was made by filling the feedthrough cavity around the power leads with liquid nitrogen, effectively cooling the catalyst crystal to temperatures as low as 140 K.

**Figure 2.2.** Catalyst crystal mounting schematic for a rectangular crystal geometry.
More importantly, sample preparation and analysis were also performed inside the UHV chamber. The deposition of vaporized reagents and precursors were introduced from a variable leak valve which is connected to a dosing line. An electron beam evaporator (Tectra) with an inline quartz crystal microbalance (QCM) were used to deposit and monitor the thickness of the metal film. What’s more, the gas content of the chamber atmosphere could be monitored with an SRS RGA200 quadrupole mass spectrometer. Alternatively, the catalyst could be lowered in the Z-direction by the adjustable manipulator into the bottom region where it could be analyzed using the HREEL spectrometer from LK technologies.

2.2.2 Temperature Programmed Desorption

Temperature programmed desorption (TPD) is the method to figure out the adsorption energies and reaction pathways of adsorbed species by increasing the surface’s temperature. Theoretically, molecules or atoms tend to minimize their energy by forming a bond with the surface when adsorbing on to it. Their binding energies vary with the combinations of the adsorbate and surface. By heating the surface, the energy transferred to the adsorbed species, which causes it to desorb at one-point, reveals information on the binding energy, adsorption interactions and surface reaction pathway. It is worthy to first mentioning the mechanics and theory of molecular adsorption and desorption from a surface.

The general procedure to perform a TPD experiment in a UHV chamber involves four main steps: (1) depositing the molecules of interest on to the single crystal surface, (2) sample was positioned in front of a small aperture in a glass shroud that enclosed the
quadrupole mass spectrometer, (3) linearly ramping the temperature of the crystal surface,
(4) the desorbing species were monitored. It is instructive to identify the theory behind the
desorption process. To begin with, the rate of desorption can be given by

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

Where \( N \) is the number of molecules adsorbed on the surface, \( m \) is the reaction
order and \( k_d \) is the desorption rate constant.

The desorption rate constant \( k_d \) can be described in the following equation

\[ k_d = A \cdot e^{-E_d/RT} \]  \hspace{1cm} (2.2)

Where \( A \) is pre-exponential constant factor, \( E_d \) is the activation energy for
desorption [kJ/mol] and \( T \) is the absolute temperature [K].

Since the heating rate is linear in time while performing TPD (a constant heating
rate of \( \frac{dT}{dt} = \beta = 3 \text{ K/s} \) was used for all TPD experiments in this thesis), we rearrange
equation 2.1 and plug in equation 2.2, the desorption rate with respect to time could be
achieved.

\[ -\frac{dN}{dT} = -\frac{dN}{dt} \cdot \frac{dt}{dT} = N^m \frac{A}{\beta} e^{-E_d/RT} \]  \hspace{1cm} (2.3)

The \( \frac{dN}{dT} \) term will be zero at \( T_p \) (temperature for desorption peak maximum), the
activation energy of the reaction can then be derived via following equation:

\[ \frac{E_d}{RT_p^\beta} = \frac{v}{\beta} e^{-E_d/RT_p} \]  \hspace{1cm} (2.4)
The equation 2.4 can be further simplified by considering that activation energy is independent of the surface coverage and the desorption kinetics are first order, which is known as Redhead Equation:

\[ E_d = RT_p = \left[ \ln \left( \frac{A}{\beta} T_p \right) \right] - 3.64 \text{ for } 10^8 < \frac{A}{\beta} < 10^{13} \]  \hspace{1cm} (2.5)

Similarly, for the second order desorption kinetics (m=2), the following expression may be derived

\[ \frac{E_d}{RT_p^2} = \frac{2Nu}{\beta} e^{-E_d/RT_p} \]  \hspace{1cm} (2.6)

The coverages of the adsorbed molecules on single crystal are quantified in unit Langmuir (symbol: L) which corresponds to the exposure of a surface to a gas at 10^{-6} torr (dosing pressure substituted the background pressure) for 1 second. The dosing pressure and time are precisely controlled to deposit the desired number of molecules to the surface. For most of TPD experiments in this thesis, a saturation coverage was used, as it would provide a better insight to the activation energy and reaction pathway than multilayer or tiny amount of reagents. The saturation coverage for molecules of interest is determined by a series of TPD experiments on Pt(111). For example, Figure 2.3 shows an example of TPD spectra. The desorption peak first grew up at 335 K at small coverage and shifted to lower temperature with increasing exposure. The emergence of “shoulder” at around 230 K is the sign of reaching the saturation coverage. Similarly, saturation coverage was determined for adsorbents used in this thesis. These data can be used to calculate the kinetic parameters of desorption of adsorbed species from a surface according to Equation 2.1-2.6. Similarly, saturation
Figure 2.3 Computer simulation of assumed 2-state flash desorption spectra of H₂ on Pt(111) at different coverage θ; — calculated curve; •, □, △, experimental data points (from [47]).

According to Equation 2.4, for first order desorption process, the activation energy ($E_d$) and the desorption temperature ($T_p$) are independent of the number of adsorbed molecules. This type of desorption that molecules remain intact and desorption is only affected by the strength of the molecules' bond with the surface, as illustrated by the peak at 335 K in Figure 2.3. With the increase of the coverage of CO, the repulsive interaction between adsorbed CO molecules decreases the adsorption energy so that the desorption temperature decreases to 250 K at higher coverages. For the second order desorption kinetics, illustrated in Equation 2.6, the desorption temperature ($T_p$) as a function of molecular coverages shift to lower temperature as coverage increases. The desorption of adsorbed molecules is associated with the dissociative adsorption, where a dissociated
molecule need recombine to desorb from the surface. With the increase of the coverages, the probability of recombination becomes greater thereby desorption temperature shift to lower temperature shown in Figure 2.4.

![Flash desorption spectra for H$_2$/Pt(111)](image)

**Figure 2.4** Set of flash desorption spectra for H$_2$/Pt(111) (from [47]).

The scheme of the residual gas analyzer (RGA) is shown in Figure 2.5. Basically, free electrons are formed by thermal emission from an electrically heated tungsten filament. Those electrons are accelerated by a potential difference (70 V) between the filament and the grid to desorbed molecules to make positive ions which are persuaded out into the rest of the machine by the ion repeller which is another metal plate carrying a slight positive charge. The quadrupole analyzer consists of four cylindrical rods held in quadrature, parallel to each other by insulating ceramic spacers. The ions are influenced by oscillating electrostatic filed generated by electrically connected opposing rods which are applied with a combination of DC and RF voltages. Only ions possessing a specific mass are able to
navigate the entire length of the quadrupole filter and are detected by a stainless-steel Faraday cup, which generates an electric current proportional to the ion current striking the cup. The low current of ions in our UHV chamber (operating pressure ~ 10^{-9} torr) makes the use of the electron multiplier a good choice. It consists of a special glass which generates a large number of secondary emission electrons upon contact with ions and can amplifies the signal of ions entering the detector.

![Diagram](image)

**Figure 2.5** Functional components of a quadrupole mass spectrometer.

2.2.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive quantitative spectroscopic technique that probe the binding energies of the electrons in the atoms near the surface and this information can be used to obtain the composition of the surface. By irradiating the X-ray to a material while simultaneously measuring the kinetic energy and number of electrons that escape from top 0-5 nm of the material, XP spectra were collected. The electron binding energy of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford (1914):
\[ E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi) \]

Where \( E_{\text{binding}} \) is the binding energy of the electron, \( E_{\text{photon}} \) is the energy of the X-ray photons being used, \( E_{\text{kinetic}} \) is the kinetic energy of the electron measured by the instrument, \( \phi \) is the working function. The work function term, \( \phi \), is defined to be the minimum energy required to remove an electron for a solid.

Core levels in XPS are defined by the terminology \( nlj \), where \( n \) is the principal quantum number, \( l \) is the angular momentum quantum number and \( j = l + s \) (where \( s \) is the spin angular momentum number and equals \( \pm 1/2 \)). For core-levels other than s-orbitals (\( l = 1 \)), they will be split into a doublet with two possible states having different binding energies due to spin-orbit splitting. Peaks will have a defined are ratio based on the degeneracy of each spin state. As shown in Figure 2.6, doublets corresponding to Nb\(^{5+}\), Nb\(^{4+}\), Nb\(^{2+}\) and Nb metal have different binding energies. This phenomenon is attributed to the fact that exact binding energy of an electron depends not only on the level from which photoemission occurs, but also on the formal oxidation state of the atom. Atoms of a higher positive oxidation state exhibit a higher binding energy due to the extra coulombic interaction between the photoemitted electron and the ion core.
Figure 2.6 XPS spectrum of the Nb 3d peaks for oxidized Nb (from [48]).

However, photoelectrons can also lose energy through inelastic collisions on their outward trajectory. Sometimes, these losses are random, they will result in the uneven baseline by increase the photoelectron intensity at binding energies. Therefore, the subtraction of baseline must be implemented before fitting any peaks to the data. Figure 2.7 shows various baseline models. In this thesis, the last model, Shirley Background was used. During curve fit, few adjustable parameters were used to obtain curve fits that were physically meaningful. The instrumental resolution (i.e. fwhm of each peak), positions of peaks, separation between two peaks and ratio of the areas of peaks were referred to literatures or the blank experiments designed by us. Those parameters were constrained with little mobility while the spectrum was fit by Gaussian-Lorentzian peaks.
Figure 2.7 Baseline reduction models for XPS peaks (from [49]).

X-ray photoelectron spectroscopy in my lab consists of a hemispherical electron energy analyzer (Leybold-Heraeus) and an X-ray source (VG Microtech) shown in Figure 2.8. X-ray source contains both Al and Mg anodes. Emitted electrons by resistively heating iridium filaments. By applying a 14 kV bias voltage, those electrons contact with X-ray sources to produce X-ray. Before contacting with sample surface, x-ray will pass an Al window which will only let x-ray to pass and prevent contamination from the filament. For both Al and Mg, the strongest emission of photons occurs when 2p electrons fill the 1s vacancy, which yields photons in the x-ray regime, with an energy of either 1486.7 eV for Al or 1253.6 eV for Mg.
Figure 2.8 Hemispherical electron energy spectrometer schematic. (from AG Jacobs)

2.2.4 High Resolution Electron Energy Loss Spectrometry

Although relative intensities and the desorption temperature of stable reactive intermediates adsorbed on the catalyst active sites can be told by TPD, more detailed insights into the reaction pathway, reaction intermediates and active sites need be obtained from surface sensitive vibrational spectroscopies, such as high resolution electron energy loss spectrometry (HREELS). HREELS operates in a similar way as infrared (IR) or Raman spectroscopy, but instead of photons, an incident beam of low-energy electrons with a known energy is scattered on a sample. The scattering of these electrons loses the energy to excite the specific vibrational structure of adsorbates on metallic substrates. Those vibrational modes are subject to the surface dipole selection rule. It states that only those vibrational modes which give rise to an oscillating dipole perpendicular to the surface are HREELS active and result in an observable absorption band. This is due to the fact that
the dynamic dipole moment generated by an oscillator that vibrates in the surface-parallel
direction is cancelled by that of its image dipole (see Figure 2.9). On the other hand, If the
real dipole is oriented perpendicularly to the surface, its dynamic dipole moment is
reinforced by that of its image dipole. The bonding configuration together with the peak
location and their relative intensity makes HREELS an informative surface sensitive
technique to provide insights to mechanism of surface reactions.

Figure 2.9 The dynamic electric moment of the dipole orientated parallel to the metal
surface is cancelled by that of its image dipole. In the vertical orientation, the dynamic electric moments of the surface and image dipoles reinforce each other (from [50]).

The vibrational spectrum obtained after exposing 4 L CO to Pt(111) surface at 150
K is shown in Figure 2.10. The C-O stretching mode peaks at 1870 cm$^{-1}$ and 2100 cm$^{-1}$ are
attributed CO adsorbed in bridge and atop Pt sites.
Figure 2.10 Vibrational spectrum obtained after ~ 4 L exposure CO on Pt(111) surface at ~ 150 K (from [51]).

The HREEL spectrometer (LK Technologies, see Figure 2.11) consists of an electron gun, a two-stage monochromator, a single-stage energy analyzer, and a channel electron multiplier detector. More generally, the electrons are generated by heating a tungsten cathode, which is encapsulated by a negatively charged repeller to prevent stray electrons from coming into the detector unit. Both energy monochromation and energy analysis are carried out with 127° cylindrical deflection analyzers. The two-stage monochromator serves to narrow the energy spread to and generate a highly monoenergetic beam of low-energy electrons (4 eV) directed at 60° with respect to the surface normal. A zoom lens system focuses and accelerates the electron beam onto the sample. The backscattered electrons are passed through a separate zoom lens for focusing and deceleration before they are sorted out by a single-stage energy analyzer into the detector. The elastic peak in each HREEL spectrum typically had an intensity in excess of $2 \times 10^4$ cps.
and a FWHM of ~40 cm\(^{-1}\). HREEL spectra were collected as a function of the sample annealing temperature. In this thesis, the reagents were dosed with the sample held at 160 K and then the sample was heated to the desired temperature and then rapidly quenched back to 160 K at which point the spectrum was collected.

Figure 2.11 (a) Schematic diagram of first-generation HREEL spectrometer; (b) Photograph of a modern ultrahigh-resolution EEL spectrometer.

2.3 High Surface Area Catalyst Studies

To bridge the gap between the surface science reaction and the real-world reaction, reaction studies on high surface area catalysts were carried out in an atmospheric tubular
reactor (see Figure 2.12). The reactor consisted of a 20-cm long stainless-steel tube with a 4.6-mm inside diameter. The reagent solution liquid feed is introduced to the reactor via a syringe pump (PHD 2000 Infusion, Harvard Apparatus). Meanwhile, the H$_2$ (UHP grade, Airgas) flow was fed to the reactor and controlled by a flow meter (Kd Scientific). For each run, 50 mg of the catalyst sample was loaded at the center of the tube between quartz-wool plugs. Various flow rate of reagents ranging from 0.02 to 0.4 mL/min was evaporated into a H$_2$ flow varying from 10 to 150 mL/min prior to contact with the catalyst bed. All of the reactant flow lines were wrapped with heating tape and held at 393 K in order to prevent condensation of the reagents. The quantitative analysis of the products was obtained using a GC-MS (QP5000, Shimadzu) calibrated using standard product solutions.

**Figure 2.12** Diagram of the atmospheric tubular reactor.
2.4 Sample Preparation

2.4.1 Monometallic Surface Preparation

A 10 mm-diameter Pt(111) single crystal (Goodfellow), with 5N purity, was used as the substrate for the UHV studies. It was initially cleaned by mechanical polishing — using typically a series of diamond pastes. Then the crystal was mounted and put into the UHV chamber. To further clean the sample and exhibit a sharp (1x1) LEED pattern, repeated cycles (6 -10 cycles) of 2 kV Ar+ ion bombardment at 1000 K for 25 min, annealing at 1150 K under 2×10⁻⁸ torr O₂ for 10 min, and annealing at 1150 K in vacuum for 5 min were carried out until no carbon was detected by XPS or HREELS. The impurities on the top of the surface can be removed by the bombardment shot by Ar⁺; annealing under O₂ would get rid of the carbon residuals on the surface and also drives the impurities in the metal lattice to segregate to the surface. Annealing under the vacuum in such a high temperature would restructure the surface back to (111) structure and exhibit a sharp (1x1) LEED pattern as described in the previous studies [52].

2.4.2 Bifunctional Catalyst Surface Preparation

For desired bifunctional catalyst, such as WOₓ-Pt(111) and NbOₓ-Pt(111) surface, a metal oxide needed to be introduced to the Pt(111) surface. Due to the high melting temperature of metallic tungsten, the traditional way to heat the target metal filament resistively does not work here. Tungsten oxide was deposited onto the Pt(111) surface using a tungsten hexacarbonyl (W(CO)₆, 99%, Strem) precursor which was contained in glass vials on stainless-steel dosing manifolds that were attached to each UHV chamber via a variable leak valve. The W(CO)₆ precursor was held at 373 K to provide sufficient vapor pressure for dosing into the UHV chamber. Each WOₓ deposition cycle consisted of
dosing the Pt(111) sample, held at 473 K, with $1 \times 10^{-8}$ torr of W(CO)$_6$ for 50 s followed by pumping for 5 min to remove any weakly adsorbed species. The sample was then annealed in $2 \times 10^{-7}$ torr of O$_2$ at 573 K for 45 min to form WO$_x$ by oxidizing the adsorbed W(CO)$_6$ precursor. The coverage of the formed tungsten oxide film was determined by the CO TPD experiments owing to the fact the CO does not adsorb strongly on metal oxide surface. The detailed calculation will be described in the results section.

However, the preparation of the NbO$_x$-Pt(111) surface is another story. As the dosing line attached to the UHV chamber cannot tolerate the temperatures higher than 375 K, and the tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) niobium(IV) (99% [Nb(TMHD)$_4$], Strem) Nb precursor is not able to reach a moderate evaporation pressure even heating to 400 K. In NbO$_x$-Pt(111) study, the metallic niobium was deposited onto the Pt(111) single crystal using an electron beam evaporator (Tectra) with a 3-mm-diameter Niobium rod source (American Elements, 99.9% purity), and the extent of Nb deposition was monitored by an in-plane QCM. All Nb coverages in this study are reported in monolayers, where one monolayer is assumed to be the density of Pt atoms on the Pt(111) surface, $1.5\times10^{15}$ atoms·cm$^{-2}$. After Nb deposition, the sample was annealed in $4\times10^{-7}$ torr of oxygen (Matheson, 99.98%) at 750 K for 1 h to form an NbO$_x$ layer.

2.4.3 High Surface Area Catalyst Preparation

Carbon supported high surface area catalysts were used for steady state reactivity studies. A 10 wt % Pt/C catalyst was prepared by incipient wetness using a tetraammineplatinum(II) nitrate Pt precursor (Pt basis 99.99%, Alfa Aesar) that was dissolved in a water/ethanol (3:1) mixture. Carbon black (225 m$^2$/g, Vulcan XC-72R) was
introduced into the precursor solution under continuous stirring. The resulting slurry was
dried in air at 333 K for 12 h and then subjected to a 2 h reduction treatment, carried out in
a continuous flow reactor with 5% H\textsubscript{2} in a 60 mL/min He carrier gas at 773 K. Atomic
layer deposition (ALD) (see Figure 2.13) was used to modify the surface of the Pt/C
catalyst with NbO\textsubscript{x} and to produce a NbO\textsubscript{x}/C catalyst. The ALD was performed using a
custom-built vacuum deposition system that has previously been described in detail[53].
An ALD deposition cycle consisted of exposing ~0.5 g of the evacuated catalyst held at
533 K to 4 torr of the tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)niobium(IV) (99%
[Nb(TMHD)	extsubscript{4}], Strem) Nb precursor for ~5 min. The sample was then heated to 637 K
while being exposed to a flowing steam of He in order to remove any weakly bound
precursor and organic ligands.[reference] It was then oxidized in air at 473 K for 30 mins
to oxidize the niobium. A single ALD cycle was used to produce the NbO\textsubscript{x}-Pt/C and
NbO\textsubscript{x}/C catalysts used in this study.

![Diagram of the atomic layer deposition](image)

**Figure 2.13** Diagram of the atomic layer deposition (Designed and built by Onn, T.M.).
Chapter 3. Active sites for the selective hydrodeoxygenation of 

\( m \)-cresol on WO\(_x\)-modified Pt

Summary

Adsorption and reaction of \( m \)-cresol on Pt(111) and WO\(_x\)-modified Pt(111) surfaces was characterized using temperature programmed desorption (TPD), high resolution electron energy loss spectroscopy (HREELS), and X-ray photoelectron spectroscopy (XPS). The results of this study show that on Pt(111) a strong interaction between the aromatic ring and the Pt surface facilitates C–C bond cleavage resulting in decomposition at relatively low temperatures. In contrast, on WO\(_x\)-modified Pt(111), \( m \)-cresol bonds to oxygen vacancy sites on the WO\(_x\) deposits via the hydroxyl oxygen with the aromatic ring tilted away from the surface, resulting in a bonding configuration that promotes selective C–O bond cleavage and limits ring hydrogenation. XPS results also show that interactions at the Pt-WO\(_x\) interface help stabilize submonolayer WO\(_x\) deposits in a partially reduced state, thereby maintaining a high concentration of the oxygen vacancy adsorption sites.
3.1 Introduction

Recently Wang et al. [42] have also reported that modifying the surface of a group 10 metal with a metal oxide can enhance the selectivity for the HDO of phenolics. Indeed, they observed that carbon-supported Pt for which the Pt surface has been decorated with WO$_{x}$ (Pt-WO$_{x}$/C) exhibited greater than 94% selectivity for the HDO of $m$-cresol to toluene for both high (36 bar) and low (1 bar) H$_2$ pressures and temperatures between 550 and 650 K. Little to no deactivation over time was also observed for these catalysts under a wide range of reaction conditions. Based on both experimental and DFT results they proposed that oxygen vacancies on the surface of the WO$_{x}$ species were the active sites for a direct C-O hydrogenolysis pathway involving $m$-cresol adsorbed via the phenolic oxygen, a bonding configuration which also prevented ring hydrogenation by limiting the interaction of the aromatic ring with the Pt surface. Furthermore, they proposed that a crucial role of the Pt was to stabilize a partially reduced WO$_{x}$ species by decreasing the barrier for oxygen vacancy formation.

The goal of the present study was to use model catalysts and ultra-high vacuum (UHV) surface sensitive spectroscopic techniques to further investigate the bonding configuration of $m$-cresol on WO$_{x}$-modified Pt and how interactions at the Pt-WO$_{x}$ interface influence the reducibility of the WO$_{x}$. In particular, we have used a procedure analogous to atomic layer deposition (ALD) to deposit WO$_{x}$ on a Pt(111) single crystal and a combination of temperature-programmed desorption (TPD) and high-resolution electron
energy loss spectroscopy (HREELS) to follow the reaction pathways and elucidate the bonding configuration of adsorbed \textit{m}-cresol. Additionally, XPS was used to investigate the reducibility of the deposited WO\textsubscript{x} species. The results of this study provide additional insight into the origins of the high selectivity of WO\textsubscript{x}-Pt for the HDO of \textit{m}-cresol.

### 3.2 Experimental

Two separate UHV apparatus with 4×10\textsuperscript{-10} torr background pressures were equipped with a quadruple mass spectrometer (SRS RGA200) for TPD and an ion sputter gun (PHI electronics) for sample cleaning. The first chamber was equipped with an HREEL spectrometer (LK Technologies), while the second was used to conduct XPS experiments and housed a hemispherical electron energy analyzer (Leybold-Heraeus) and an Al K\textalpha{} X-ray source (VG Microtech). The Pt(111) surface was cleaned by repeated cycles of 2 kV Ar\textsuperscript{+} ion bombardment at 600 K for 45 min, annealing at 1150 K under 2×10\textsuperscript{-8} torr O\textsubscript{2} for 10 min, and annealed at 1150 K in vacuum for 5 min until no carbon was detected by XPS or HREELS. We have previously shown that this procedure also produces a surface which exhibits a sharp (1×1) LEED pattern [52,54].

Tungsten oxide was deposited onto the Pt(111) surface using a tungsten hexacarbonyl (W(CO)\textsubscript{6}, 99%, Strem) precursor which was contained in glass vials on stainless-steel dosing manifolds that were attached to each UHV chamber via a variable leak valve. The W(CO)\textsubscript{6} precursor was held at 373 K to provide sufficient vapor pressure for dosing into the UHV chamber. Each WO\textsubscript{x} deposition cycle consisted of dosing the Pt(111) sample, held at 473 K, with 1×10\textsuperscript{-8} torr of W(CO)\textsubscript{6} for 50s followed by pumping
for 5 min to remove any weakly adsorbed species. The sample was then annealed in $2 \times 10^{-7}$ torr of O$_2$ at 573 K for 45 min to form WO$_x$ by oxidizing the adsorbed W(CO)$_6$ precursor.

The m-Cresol (Alfa Aesar, 99%) reactant was contained in glass vials that were also attached to the stainless-steel dosing manifolds. Each TPD experiment consisted of dosing the Pt(111) sample, held at 160 K, with m-cresol at the desired pressure and duration. After dosing m-cresol, the sample was positioned in front of a small aperture in a glass shroud that enclosed the quadrupole mass spectrometer and then heated at 3 K•s$^{-1}$ while the desorbing species were monitored. Multiple m/z ratios were monitored during each TPD run to ensure accurate identification of all products. Coverage variation experiments showed that a 0.6 L dose (1 L=10$^{-6}$ torr•s) was sufficient to saturate the surface and this dose was used in all of the TPD and HREELS experiments reported.

3.3 Results

3.3.1 Characterization of WO$_x$ deposition

The procedure used in this study to decorate the Pt(111) surface with WO$_x$ using a W(CO)$_6$ precursor as described in the experimental section was chosen to mimic the ALD process that was used in previous studies of WO$_x$-modified supported Pt catalysts [42,53]. Both XPS and CO TPD were used to characterize the WO$_x$ deposition on the Pt(111) surface. W(4f) XPS spectra for (a) the Pt(111) surface dosed with the W(CO)$_6$ precursor at 160 K and (b) after oxidation of the dosed-surface in $2 \times 10^{-7}$ torr of O$_2$ at 573 K for 45 min are displayed in Fig 3.1. The spectrum of the as-dosed surface contains peaks at 31.2 eV and 33.3 eV that can be assigned to the W(4f$_{7/2}$) and W(4f$_{5/2}$) doublet. These peak positions are consistent with zero-valent W and are close to those reported for W(CO)$_6$ adsorbed on
Ni(100) [55,56]. The spectrum obtained following oxidation is more complex and consists of multiple overlapping peaks between 30 and 40 eV. As shown in the figure this spectrum can be curve resolved into three doublets corresponding to W\(^{4+}\), W\(^{5+}\) and W\(^{6+}\). The percent of each W oxidation state, as determined from the peak areas, is given in Table 3.1. Note that for these conditions only 22% of the W is completely oxidized to W\(^{6+}\) with the majority, 54%, being W\(^{4+}\). The corresponding C(1s) spectra are displayed in Figure 3.1. The C(1s) spectrum for the adsorbed W(CO)\(_6\) precursor prior to the oxidation treatment contains a peak at 287 eV and a much smaller peak at 293 eV. This spectrum is similar to that reported in previous studies of W(CO)\(_6\) adsorbed on several other surfaces where the latter peak has been attributed to a shake-up feature [56–58]. After the oxidation treatment, the C(1s) spectrum contains a single small peak at 284 eV which can be attributed to CO adsorbed on bare portions of the Pt(111) surface which likely adsorbed from the chamber background gas during the time it took to collect the XPS spectrum. This result demonstrates that complete decarbonylation of the tungsten precursor occurred during the oxidation treatment.
**Figure 3.1** C(1s) XPS spectra for (a) tungsten hexacarbonyl dosed on Pt(111) and (b) after oxidization.

![C(1s) XPS spectra](image)

**Figure 3.2** W(4f) XPS spectra for (a) the Pt(111) surface dosed with W(CO)$_6$ precursor at 160 K and (b) after oxidization in 2×10$^{-7}$ torr of O$_2$ at 573 K for 45 min.

![W(4f) XPS spectra](image)

<table>
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<th>Sample</th>
<th>W$^{4+}$</th>
<th>W$^{5+}$</th>
<th>W$^{6+}$</th>
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<td>WO$_x$/Pt(111)</td>
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<td>24%</td>
<td>22%</td>
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<td>26%</td>
<td>24%</td>
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<tr>
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<td>$m$-cresol-WO$_x$/Pt(111) 450 K</td>
<td>57%</td>
<td>19%</td>
<td>24%</td>
</tr>
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</table>

**Table 3.1** Area percentages of W(4f) XPS peaks for different numbers of WO$_x$ deposition cycles and for WO$_x$/Pt(111) dosed with 0.6 L $m$-cresol at 160 K and after heating to 450 K.
Thermodynamic calculations based on Gibbs free energies for the formation of tungsten oxides by Wang et al. [42] predict that for a $P_{O_2}$ of $2 \times 10^{-7}$ torr and 573 K, the conditions used to prepare the WO$_x$/Pt(111) sample, tungsten should be in its fully oxidized form, WO$_3$. Thus, it is somewhat surprising that the XPS data (see Figure 3.2) show that a range of sub-oxide, WO$_x$, species are present on the surface. This observation suggests that interaction of the WO$_x$ with the Pt(111) surface helps to stabilize the sub-oxides. To further explore this possibility XPS spectra were collected as a function of the number of WO$_x$ deposition cycles. Figure 3.3 compares the W(4f) spectra obtained following 1, 3, and 6 deposition cycles (denoted as WO$_x$/Pt(111), (3R)-WO$_x$/Pt(111) and (6R)-WO$_x$/Pt(111)) and the percent of each W oxidation state in each spectrum, as determined via curve resolution, are reported in Table 3.1. As will be discussed below, each cycle deposits ~0.4 ML of WO$_x$, thus, these data range from sub-monolayer to slightly greater than two monolayer WO$_x$ coverages. The spectra in Figure 3.3 clearly show an increase in intensity at the higher binding energies with increasing number of WO$_x$ deposition cycles. Thus, the average oxidation state of the W in the WO$_x$ film increases with WO$_x$ coverage or film thickness. The quantitative analysis of the data in Table 3.1 shows that the faction W$^{6+}$ in the film increased from 22% to 32% in going from one round to six rounds of WO$_x$ deposition. These results provide additional evidence that interactions at the Pt-WO$_x$ interface help stabilize the lower W oxidation states.
Figure 3.3 W(4f) XPS spectra after (a) one (b) three, and (c) six WO$_x$ deposition cycles.

CO TPD was used to determine the coverage of the WO$_x$ film as a function of the number of deposition cycles. Figure 3.4 displays TPD data obtained from the WO$_x$/Pt(111) surface dosed with 1 L (saturation dose [59]) of CO at 160 K as a function of the number of WO$_x$ dosing/oxidation cycles. The blue spectrum corresponds to the clean Pt(111) surface and contains the expected intense peak at 440 K corresponding to desorption of CO from Pt atop sites [60]. Following one WO$_x$ deposition cycle the CO desorption peak (black curve) decreased in intensity somewhat and shifted down to 420 K. Based on a comparison
of the CO peak areas for these two samples, we estimate that the WO\textsubscript{x} coverage is ~0.4 ML. As shown in the figure, additional WO\textsubscript{x} deposition cycles resulted in further decreases in the both the CO peak area and temperature, and after only three cycles the CO peak area was less than 8% of that on the clean Pt(111). This result also demonstrates that the CO does not adsorb strongly on the WO\textsubscript{x}. Since one goal of this study was to investigate any synergistic effects between Pt and WO\textsubscript{x} sites, for the \textit{m}-cresol reactivity studies reported below, one round of WO\textsubscript{x} deposition was used.

HREELS was also used to characterize the WO\textsubscript{x} film produced by one deposition cycle. The low wavenumber region the HREEL spectrum of the WO\textsubscript{x}/Pt(111) sample which contains the vibrational features associated with the WO\textsubscript{x} film are shown in Figure 3.5. A comparison to the IR and Raman spectra [61] of WO\textsubscript{3} suggests that the peaks at 225 cm\textsuperscript{-1} and 920 cm\textsuperscript{-1} are due to $\square$(W-O-W) and $\square$(W=O) modes, respectively. The small peak near 610 cm\textsuperscript{-1} is likely due to a $\square$(O-W-O) mode, while the origin of the broad peak at 490 cm\textsuperscript{-1} is less clear.
3.2 Reaction of \textit{m}-Cresol on Pt(111)

TPD was initially used to provide insight into the adsorption and reaction of \textit{m}-cresol on the WO$_x$-free Pt(111) surface. These data are displayed in Figure 3.6 and show that weakly bound \textit{m}-cresol desorbs at 245 K and that H$_2$ and CO, the only gaseous reaction products, desorb in multiple peaks between 300 and 750 K. The H$_2$ peaks were primarily centered at 350 K and 535 K, with a much broader feature spanning from 610 K to 760 K. The peak at 350 K is characteristic of the recombinative desorption of H atoms from Pt(111) [62] and thus demonstrates that scission of either the O-H or some of the C-H bonds in the adsorbed \textit{m}-cresol has already occurred by this temperature. CO was produced in two distinct peaks centered at 460 K and 535 K, with a smaller, less distinct peak between 560 K and 650 K. The CO peak at 460 K is at the same temperature as that expected for
desorption-limited CO from Pt(111) [62]. The simultaneous desorption of H₂ and CO at 535 K indicates a reaction limited process.

Figure 3.6 TPD spectra obtained following exposure of the Pt(111) surface to 0.6 L of m-cresol.

HREELS was used to identify adsorbed intermediates formed from reaction of m-cresol on the Pt(111) surface. Figure 3.7 shows the HREELS vibrational spectra as a function of temperature for Pt(111) dosed with 0.6 L m-cresol at 160 K. As noted above, the spectra corresponding to higher temperatures were obtained by briefly heating the sample to the indicated temperature and then letting it cool back to 160 K, at which point the spectrum was collected. The peaks in the spectrum obtained after dosing on Pt (111) surface at 160 K are consistent with the IR and Raman spectra of molecular m-cresol [63–65]. Individual peak assignments are given in Table 3.2.
Table 3.2 Vibrational mode assignments of \( m \)-cresol on Pt(111) and WO\(_x\)/Pt(111) surface

Heating the \( m \)-cresol-dosed Pt(111) surface to 200 K and 245 K produced relatively minor changes in the HREEL spectrum. The latter temperature is sufficient to desorb weakly bond molecule \( m \)-cresol as demonstrated by the TPD data. The primary differences in the spectrum at 245 K relative to that at 160 K are a decrease in the intensities of the \( \nu(C-H) \) peaks (2950 and 3000 cm\(^{-1}\)), the CH\(_3\) out of plane rocking mode (1150 cm\(^{-1}\)), and the \( \beta(O-H) \) peak (1270 cm\(^{-1}\)). The broad, hydrogen-bonded, \( \nu(O-H) \) feature in the spectrum between 3100 and 3500 cm\(^{-1}\) at 165 K also sharpens into a single \( \nu(O-H) \) peak at 3240 cm\(^{-1}\) upon heating to 200 K and is nearly absent at 245 K. The low intensity of the \( \nu(C-H) \) peaks of the aromatic ring at 3000 cm\(^{-1}\) in the 245 K spectrum suggests that the aromatic ring is positioned parallel to the surface in chemisorbed \( m \)-cresol, since for this

<table>
<thead>
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<th>Mode</th>
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<td></td>
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</table>

\( \nu \); stretching, \( \beta \); in-plane bending, \( \gamma \); out-of-plane bending, \( \tau \); torsion, \( \tau \); twisting, \( \nu \); in-plane-rocking, \( \nu \); out-plane-rocking.
configuration the induced image dipoles in the metal would decrease the cross-sections for exciting these modes. While this conclusion is not definitive, it is consistent with previous studies that have demonstrated that the $\pi$-electron system in aromatic rings (e.g. benzene [66,67], phenol [68,69] and benzaldehyde [70]) interact strongly with the metal d-band on Pt(111) resulting in an adsorption configuration in which the aromatic ring lies parallel to the surface. The DFT studies of the interaction of $m$-cresol with Pt(111) reported by Tan et al. [71] also indicate that $m$-cresol adsorbs flat on bridge sites on Pt(111) through the aromatic ring carbons. In this configuration the hydroxyl group does not interact with metal surface owing to the rather long Pt-O distance.

Figure 3.7 HREEL vibrational spectra as a function of temperature for Pt(111) dosed with 0.6 L $m$-cresol at 160 K.
Heating to 300 K led to significant changes in the HREEL spectrum. By this temperature the $\nu$(O-H) mode is completely absent indicating dissociation of the O-H group has occurred. Dramatic changes in the C-H bending region are also apparent, including a large diminution in the intensity of the out-of-plane bending mode at 785 cm$^{-1}$, an increase in intensity of the in-plane bending mode at 860 cm$^{-1}$, and the near disappearance of the CH$_3$ out-of-plane rocking mode at 1150 cm$^{-1}$. Based on this spectrum alone, we are not able to unambiguously identify the adsorbed specie(s) that are present on the surface at this temperature. It is clear, however, that decomposition the adsorbed m-cresol has started to occur. This conclusion is supported by the decrease in the intensity of the aliphatic $\nu$\(_{\text{ring}}$(C-H) mode peak at 3000 cm$^{-1}$ relative to that of the $\nu$\(_{\text{methyl}}$(C-H) peak at 2950 cm$^{-1}$, which indicates a loss of aromaticity in at least some of the adsorbed intermediates, and by the appearance of peaks in the C-O stretching region at 1750 and 2000 cm$^{-1}$. These latter peaks, which can be assigned to CO adsorbed in bridge and atop Pt sites, respectively, are a little lower in energy than that typically observed for CO on Pt(111). This can be attributed to interaction of the remaining electron-donating aromatic rings with the surface which enhances the back donation of electrons from the Pt d orbitals into the 2\pi* anti-bonding orbitals of the adsorbed CO. This effect is typically observed for CO on Pt(111) when co-adsorbed with aromatic molecules [72].

The HREELS data at 350 K and higher just indicate further unselective decomposition of the adsorbed species which is consistent with the TPD data that contains reaction-limited H$_2$ and CO peaks between 400 and 600 K. It is noteworthy that by 500 K the bridge and atop â€œ(C-O) peaks of adsorbed CO have shifted up in energy to 1850 and
2100 cm\(^{-1}\) which is consistent with decomposition of the remainder of the adsorbed aromatic rings [73]. Concomitant with this shift in energy is the appearance of a prominent peak at 480 cm\(^{-1}\) which can be attributed to a Pt-C stretch [40,41] associated with carbon atoms or small hydrocarbon fragments adsorbed on the surface.

3.3. Reaction of \(m\)-Cresol on WO\(_x\)/Pt(111)

Similar to our previous studies of Zn- and Co-decorated Pt(111) surfaces [40,70,74], the addition of WO\(_x\) to Pt(111) significantly altered the interaction of the \(m\)-cresol with the surface. This is evident in the TPD data obtained from 0.4 ML WO\(_x\)/Pt(111) dosed with 0.6 L of \(m\)-cresol which is displayed in Figure 3.8. The low-temperature \(m\)-cresol desorption feature is similar to that from the WO\(_x\)-free Pt(111) surface and H\(_2\) and CO were again the only reaction products observed with H\(_2\) desorbing in three distinct peaks centered at 350 K, 430 K and 540 K, and CO primarily in a peak centered at 430 K, with a smaller peak at 540 K. The features at 540 K are reaction limited, similar to those observed for Pt(111), and can be attributed to unselective decomposition of adsorbed intermediates. Differences are observed, however, in the lower-temperature region of the TPD spectra from the Pt(111) and WO\(_x\)/Pt(111) surfaces. In particular, for the WO\(_x\)/Pt(111) surface relatively little hydrogen is produced between 300 and 500 K, while the H\(_2\) desorption curve for Pt(111) is dominated by a large peak at 350 K. This demonstrates that dehydrogenation of \(m\)-cresol (or an \(m\)-cresol-derived species) occurs at much higher temperatures on the WO\(_x\)-modified surface relative to the clean surface; however, the large CO peak at 430 K for WO\(_x\)/Pt(111) is at a temperature close to that expected for desorption-limited CO from Pt(111) [62] and indicates that significant reaction/decomposition of the \(m\)-cresol has occurred by this temperature.
Figure 3.8 TPD spectra obtained following exposure of the WO₅/Pt(111) surface to 0.6 L of m-cresol.

*m*-Cresol TPD experiments were also performed using a WO₅/Pt(111) sample for which the WO₅ coverage was in excess of a monolayer. For these experiments it was observed that the surface was much less reactive with the majority of the *m*-cresol desorbing intact below 300 K.
Figure 3.9 HREEL vibrational spectra of a function of temperature for WO₅/Pt(111) dosed with 0.6 L m-cresol at 160 K.

HREEL spectra as a function of temperatures for a 0.4 ML WO₅/Pt(111) dosed with 0.6 L m-cresol are shown in Figure 3.9. The spectra at and below 220 K are nearly identical to that obtained from m-cresol-dosed WO₅-free Pt(111) in the same temperature range and are consistent with the IR and Raman spectra for m-cresol as shown in Table 3.1 [63–65]. Except for the appearance of a peak at 490 cm⁻¹ which is likely associated with the WO₅ species, heating to 275 K, which is sufficient to desorb any weakly physisorbed m-cresol, mostly produced changes in the relative peak intensities in the spectrum, such as an increase in the intensity of the 1150 cm⁻¹ CH₃ outplane-rocking (OPR) mode relative to the 750 cm⁻¹ γ(C-H) mode, and in the methyl C-H deformation region where there is an increase in the intensity of the symmetric δCH₃ peak at 1380 cm⁻¹ relative to the asymmetric
δ_{CH3} peak at 1430 cm\(^{-1}\). These latter changes suggest that, on average, the methyl groups have become oriented closer to the surface normal at 275 K [75], indicating that the \(m\)-cresol tends to bond to the WO\(_x/Pt\)(111) surface in a configuration in which the aromatic ring is tilted away from the surface. This is also consistent with the persistence of both the aliphatic and aromatic C-H stretching modes at 2890 and 3000 cm\(^{-1}\). It is noteworthy that the ν(O-H) peak at 3260 cm\(^{-1}\) is still resolvable in this spectrum.

![HREELS vibrational spectra of WO\(_x/Pt\)(111) and intermediate on WO\(_x/Pt\)(111) surface formed from \(m\)-cresol.]

Figure 3.10 HREELS vibrational spectra of WO\(_x/Pt\)(111) and intermediate on WO\(_x/Pt\)(111) surface formed from \(m\)-cresol.

One notable feature in the spectrum at 400 K is the emergence of a peak at 390 cm\(^{-1}\). This is more apparent in Figure 3.10 which provides an expanded view of this region of the spectra for \(m\)-cresol-dosed WO\(_x/Pt\)(111) at 275, 350, and 400 K. Metal-carbon and metal-oxygen stretching modes typically appear in this low-energy region of the spectrum.
[76–78], for example, one of the WO₅ modes is centered at 490 cm⁻¹. Since a peak near 390 cm⁻¹ does not appear in the spectra of m-cresol-dosed Pt(111), this peak does not appear to be due to a Pt-C stretch (note that we assign the peak at 480 cm⁻¹ in the Pt(111) spectra to ν(Pt-C)). It is possible that the 390 cm⁻¹ peak is due to a W-O stretch, but the spectrum of the as-deposited WO₅ species also does not contain such a peak. We therefore tentatively assign this peak to a ν(W-C) stretching mode.

Upon heating to 400 K there is also some diminution of the intensity of the ν(C-O) peak at 1010 cm⁻¹ (see Figure 3.9) which suggests that cleavage of the C-O bond in the adsorbed m-cresol may have occurred, at least for a portion of the adsorbed species. The persistence of the ν(C-H) peak at 3000 cm⁻¹, however, demonstrates that the aromatic character of the adsorbed species is maintained. This is in contrast to the HREELS data for m-cresol on Pt(111) which showed significant decomposition of the m-cresol occurs by this temperature. Unfortunately, the fact that there are likely to be several adsorbed species on the surface at this temperature, coupled with the relatively low quality of the HREEL spectrum it is not possible to assign the spectrum of the m-cresol-dosed WO₅/Pt(111) at 400 K to specific adsorbed species.

Heating the m-cresol-dosed WO₅/Pt(111) surface above 400 K resulted in decomposition of the adsorbed intermediates and by 650 K the spectrum was dominated by the low-energy stretching modes of the WO₅ deposits, bridge and atop (C-O) peaks at 1800 and 2020 cm⁻¹ of adsorbed CO, and a broad ν(C-H) stretch at 2900 cm⁻¹. It is noteworthy that the C-O stretching modes have shifted up in energy and are now closer to
those expected for CO on clean Pt(111) which is consistent with the loss of the aromatic character of the adsorbed hydrocarbon fragments which remain on the surface.

To investigate the possibility that the W in the WOₓ deposits on the Pt(111) surface act as redox sites, XPS was used to monitor changes in the W oxidation state upon exposure to m-cresol. Figure 3.111 displays the XPS spectra of m-cresol-dosed WOₓ/Pt(111) at 160 K and after heating to 450 K. Except for a decrease in the signal strength the spectrum at 160 K is nearly identical to that obtained for the as-prepared WOₓ/Pt(111) sample (see Figure 3.2) containing W⁴⁺, W⁵⁺, and W⁶⁺, and as shown in Table 3.1 the percent of each oxidation state is close to that obtained from the un-dosed sample; however, heating the m-cresol-dosed sample to 450 K induced significant changes in the W(4f) spectrum with the intensity of W⁶⁺ doublet increasing relative to those for W⁴⁺ and W⁵⁺. The changes in the amount of each oxidation state are quantified in Table 3.1. This result suggests under-coordinated W cations (or oxygen vacancies) are adsorption sites for m-cresol with binding occurring via the hydroxyl oxygen.
Figure 3.1 W(4f) XPS spectra for m-cresol adsorbed on WOₓ/Pt(111) surface at (a) 160 K and (b) after heating to 450 K.

3.4 Discussion

As noted in the introduction, WOₓ-Pt/C catalysts exhibit unusually high activity and selectivity for the HDO of m-cresol to produce toluene [42]. This contrasts with unmodified Pt/C, which in addition to toluene, produces a high fraction of products in which the aromatic ring has been saturated [24,79]. For Pt/C it has been proposed that HDO proceeds along a pathway that involves partial hydrogenation of the aromatic ring followed by C-OH bond hydrogenolysis. A subsequent dehydrogenation step is then required to produce toluene [80]. For WOₓ-Pt/C Wang et al. [42] have proposed HDO occurs in a more direct manner that proceeds via C-O bond hydrogenolysis in m-cresol adsorbed on an oxygen vacancy site on the WOₓ. Their DFT calculations indicate that interactions at the WOₓ-Pt interface help maintain the WOₓ in a partially reduced state, thereby providing a high concentration of the active redox sites.
The results obtained in the present study for a model WO\textsubscript{x}/Pt(111) catalyst provide more definitive evidence for the conclusion that Pt helps maintain the oxygen vacancy or redox sites on the surface of the WO\textsubscript{x} deposits. Tungsten trioxide is a stable oxide and even for the relatively mild oxidation conditions used here, the free energies for oxide formation predict that the tungsten should be in its fully oxidized form, \textit{i.e.} WO\textsubscript{3}. The XPS data in Figure 3.2 and Table 3.1, however, show that this is not the case for a submonolayer WO\textsubscript{x} film on Pt(111) which contains a mixture of W\textsuperscript{4+}, W\textsuperscript{5+}, and W\textsuperscript{6+}. The XPS data in Figure 3.3 and Table 3.1 also show that the fraction of tungsten in the +6 oxidation state increases with increasing film thickness, again indicating that interactions at the Pt-WO\textsubscript{x} film appear to help maintain the submonolayer WO\textsubscript{x} deposits in a partially reduced state.

Evidence that adsorption and reaction of \textit{m}-cresol occurs on the partially reduced tungsten sites is provided by the XPS data for an \textit{m}-cresol-dosed WO\textsubscript{x}/Pt(111) sample (Figure 3.11) which shows that the reaction of the \textit{m}-cresol results in further oxidation of the WO\textsubscript{x}, consistent with a redox type mechanism. Furthermore, the reactivity of the WO\textsubscript{x}-Pt(111) surface towards \textit{m}-cresol decreased substantially for WO\textsubscript{x} coverages greater than one monolayer where \textit{m}-cresol desorbed largely intact at temperatures below 300. This result is also consistent with a previous study of the reactivity of high surface area WO\textsubscript{x}-Pt/C catalysts that were synthesized using ALD [53].

The HREELS data (Figures 3.7 and 3.9) also demonstrate significant differences in the reaction pathways for \textit{m}-cresol on Pt(111) and WO\textsubscript{x}/Pt(111). Consistent with previous studies of functionalized aromatics on Pt(111) [66–70], the HREEL spectra of \textit{m}-cresol on this surface indicate a strong interaction between the Pt and the aromatic ring resulting in
a bonding configuration where the ring lays flat on the surface. Under typical HDO reaction conditions where high H$_2$ pressures are used, this bonding configuration would be expected to facilitate ring hydrogenation as is observed experimentally [42]. The HREELS data also indicates that dissociation of the O-H bond in the $m$-cresol occurs below 250 K. Under the UHV conditions investigated here, this adsorbed phenoxy species decomposes at relatively low temperatures with loss of the aromatic character of the ring occurring below 350 K.

In contrast to Pt(111) and in concurrence with the DFT calculations of Wang et al. [42] the HREELS and XPS data obtained here indicate that on WO$_x$/Pt(111) $m$-cresol adsorbs molecularly on undercoordinated W cation sites via the hydroxyl oxygen resulting in a more upright bonding configuration in which the aromatic ring is tilted away from the surface as shown schematically in Figure 3.12. This molecular species exhibits much higher thermal stability than the corresponding phenoxy species on Pt(111) remaining intact up to 400 K. The lack of covalent bonding between the aromatic ring and the surface would be expected to suppress both ring hydrogenation and ring opening, thereby facilitating the selective C-O bond scission as reported by Luo et al. [81]. For the UHV conditions used here, this adsorbed species ultimately decomposes, but under more realistic HDO reaction conditions this species likely undergoes C-O bond hydrogenolysis to form toluene as predicted by the previous DFT results.
Figure 3.12 Proposed pathways and intermediates for the adsorption and reaction of m-
cresol on WO<sub>x</sub>/Pt(111).

3.5 Conclusions

The results of this study provide experimental confirmation of the DFT predictions of Wang et al. [42] that interactions at the Pt-WO<sub>x</sub> interface enhance the reducibility of submonolayer WO<sub>x</sub> deposits and help maintain them in a partially reduced state and that m-
cresol adsorbs on undercoordinated W cations in the supported WO<sub>x</sub> via the hydroxyl oxygen in a bonding configuration in which the aromatic ring is tilted away from the surface. The weak interaction between aromatic ring and Pt surface enhances the selectivity for C-O bond scission and would also limit ring hydrogenation under typical HDO reaction conditions.

Chapter 4 Direct Hydrodeoxygenation of m-Cresol to Toluene over Bifunctional NbO<sub>x</sub>–Pt

Summary

This study compared the hydrodeoxygenation (HDO) of m-cresol over Pt and NbO<sub>x</sub>-modified Pt catalysts. Reactivity measurements demonstrated that Pt supported on carbon (Pt/C) has moderate selectivity for the production of toluene during the HDO of m-
cresol, with a range of ring saturation products also being produced. The modification of Pt with niobium (NbO\textsubscript{x}–Pt/C), however, was found to enhance the selectivity to toluene to 95%. Temperature-programmed desorption, X-ray photoelectron spectroscopy, and high-resolution electron energy loss spectroscopy studies of model Pt(111) single crystal catalysts were used to provide insight into the mechanism by which the niobium enhances the selectivity. These studies showed that interactions at the NbO\textsubscript{x}–Pt interface help maintain the niobium in a partially reduced state that contains unsaturated Nb cations, which provide adsorption sites on which \textit{m}-cresol undergoes direct C–O bond hydrogenolysis to produce toluene.

### 4.1 Introduction

In chapter 3, it was found that WO\textsubscript{x}-modified Pt exhibits an extremely high selectivity and activity from \textit{m}-cresol to desired toluene. Similarly, NbO\textsubscript{x} has been reported to modify the HDO reaction pathway of aromatic oxygenates. For example, Guo et al. [43] have reported that Ru modified by Nb\textsubscript{2}O\textsubscript{5} shows a high selectivity for the HDO of \textit{p}-cresol to produce
toluene when 2-propanol is used as a hydrogen donor. In these studies, it was concluded that the reaction proceeds via a direct hydrogenolysis pathway. These studies also demonstrate that metal oxides can be quite effective in modifying the selectivity of HDO catalysts.

In the work reported here, we have expanded our previous mechanistic studies of the use of oxides to enhance the selectivity of Pt-based catalysts for the HDO of aromatic oxygenates to produce aromatic hydrocarbons and to include the use of niobium oxide as the oxide modifier. Atmospheric pressure flow reactor measurements using high surface area NbOₓ–Pt/C catalysts are presented, which demonstrate the high HDO selectivity of this catalyst for the HDO of m-cresol to produce toluene. Ultrahigh vacuum (UHV) surface science studies of model single crystal Pt(111) and NbOₓ/Pt(111) catalysts are also presented. In these latter studies we used a combination of temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high-resolution electron energy loss spectroscopy (HREELS) to elucidate both the reaction pathways and the mechanism by which the niobium modifies the reactivity.

4.2 Experimental

4.2.1 High Surface Area Catalysts

Carbon-supported high surface area catalysts were used for steady-state reactivity studies. A 10 wt % Pt/C catalyst was prepared by incipient wetness using a tetra-ammineplatinum(II) nitrate Pt precursor (Pt basis 99.99%, Alfa Aesar) that was dissolved
in a water/ethanol (3:1) mixture. Carbon black (225 m\textsuperscript{2}/g, Vulcan XC-72R) was introduced into the precursor solution under continuous stirring. The resulting slurry was dried in air at 333 K for 12 h and then subjected to a 2 h reduction treatment, carried out in a continuous flow reactor with 5% H\textsubscript{2} in a 60 mL/min He carrier gas at 773 K. Atomic layer deposition (ALD) was used to modify the surface of the Pt/C catalyst with NbO\textsubscript{x} and to produce a NbO\textsubscript{x}/C catalyst. The ALD was performed using a custom-built vacuum deposition system that has previously been described in detail [53]. An ALD deposition cycle consisted of exposing ~0.5 g of the evacuated catalyst held at 533 K to 4 Torr of the tetakis(2,2,6,6-tetramethyl-3,5-heptanedionato)niobium(IV) (99% [Nb–(TMHD)	extsubscript{4}], Strem) Nb precursor for ~5 min. The sample was then heated to 637 K while being exposed to a flowing steam of He in order to remove any weakly bound precursor and organic ligands [82]. It was then oxidized in air at 473 K for 30 min to oxidize the niobium. A single ALD cycle was used to produce the NbO\textsubscript{x}−Pt/C and NbO\textsubscript{x}/C catalysts used in this study.

Reactivity studies were carried out using a tubular reactor, operating at 1 bar of total pressure. The reactor consisted of a 20 cm long stainless-steel tube with a 4.6 mm inner diameter. For each run, 50 mg of the catalyst sample was loaded at the center of the tube between quartz-wool plugs. Then, 0.05 mL/min of \textit{m}-cresol liquid was evaporated into a 100 mL/min of H\textsubscript{2} flow prior to contact with the catalyst bed. All of the reactant flow lines were wrapped with heating tape and held at 393 K in order to prevent condensation of the \textit{m}-cresol. The quantitative analysis of the products was obtained using a GC-MS (QP5000, Shimadzu) calibrated using standard product solutions.
4.2.2 Model Catalysts

Temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), and high-resolution electron energy loss spectroscopy (HREELS) experiments were conducted in two separate UHV apparatus with $4 \times 10^{-10}$ Torr of background pressure, as reported in previous studies [41,74,83,84]. Both chambers were equipped with a quadruple mass spectrometer (SRS RGA200) for TPD, an ion sputter gun (PHI electronics) for sample cleaning, and an electron beam evaporator (Tectra) for metal deposition. One chamber was equipped with an HREEL spectrometer (LK Technologies), while the other was used to conduct XPS experiments and housed a hemispherical electron energy analyzer (Leybold-Heraeus) and an Al Kα X-ray source (VG Microtech). The Pt(111) surface was cleaned by repeated cycles of bombarding 2 kV Ar⁺ ions at 1000 K for 25 min, annealing at 1150 K under $2 \times 10^{-8}$ Torr of O₂ for 10 min, and annealing at 1150 K in vacuum for 5 min, until no carbon was detected by XPS or HREELS. We have previously shown that this procedure produces a surface which exhibits a sharp (1 × 1) low-energy electron diffraction (LEED) pattern [52,54].

For the UHV studies, niobium was deposited onto the Pt(111) single crystal using an electron beam evaporator (Tectra) with a 3 mm diameter Niobium rod source (American Elements, 99.9% purity), and the extent of Nb deposition was monitored by an in-plane QCM. All Nb coverages in this study are reported in monolayers, where one monolayer (ML) is assumed to be the density of Pt atoms on the Pt(111) surface, $1.5 \times 10^{15}$ atoms/cm². After Nb deposition, the sample was annealed in $4 \times 10^{-7}$ Torr of oxygen (Matheson, 99.98%) at 750 K for 1 h to form an NbOₓ layer.
4.3 Results

4.3.1 Steady-state Reactivity Studies

The initial investigations focused on steady state, flow reactor studies of the reactivity of the high surface area Pt/C catalysts for the HDO of $m$-cresol. In particular, the selectivity for the production of the desired HDO product, toluene, was measured for reaction in the gas phase using a reactant stream containing 1 mol% $m$-cresol and the balance $\text{H}_2$ at a total pressure of 1 bar, a temperature of 623 K, and a WHSV of 6 h$^{-1}$. Conversion and the product selectivity obtained in these experiments for both the Pt/C and NbO$_x$-Pt/C catalysts are presented in Figure 4.1. For comparison, the reactivity of the NbO$_x$/C catalyst was also measured but was found to be totally inactive for these reaction conditions. As shown in the Figure 4.1, the Pt/C catalyst was reasonably selective for the production of toluene (TOL) exhibiting a 68 % selectivity for this product. A range of products in which the aromatic ring had been saturated were also produced, however, including 3-methylcyclohexanol (OL, 6%), 3-methylcyclohexanone (ONE, 12%), as well as the hydrogenation/dehydration product methylcyclohexane (MCH, 14%). Significantly different results were obtained for the niobium-modified catalyst which was almost twice as active and exhibited 95 % selectivity for the production of the desired toluene product with a small amount of methylcyclohexane being the only other product detected.

The difference in the selectivity for Pt/C and NbO$_x$-Pt/C along with the complete inactivity of NbO$_x$/C suggests that for the NbO$_x$-Pt/C initial activation of the $m$-cresol must occur on the Pt with subsequent reactions involving the NbO$_x$, or there are synergistic interactions between the niobium and platinum that produce active sites that are not present in the Pt-only and niobium-only catalysts. The results obtained here for the high surface
catalysts are similar to those reported previously for WO$_x$-modified Pt/C [42]. As noted in the introduction, for WO$_x$-Pt/C it has been suggested that direct HDO of $m$-cresol occurs on partially reduced cation sites on the Pt-supported WO$_x$ layer with interactions at the WO$_x$-Pt interface helping to keep the tungsten in a partially reduced active state [45]. The model catalyst studies that are described in the next section were undertaken in order to determine if a similar effect is important for the NbO$_x$-Pt system.

![Figure 4.1](image.png)

**Figure 4.1** Conversion and selectivity for HDO of $m$-cresol over NbO$_x$-Pt/C, Pt/C and NbO$_x$/C catalysts. Reaction conditions: 623 K, 1 bar total pressure, 1 mol% $m$-cresol and balance H$_2$ with a flow rate of 100 mL/min and WHSV = 6 h$^{-1}$.

4.3.2 Model catalyst studies

This section describes Pt(111) model catalyst studies that focused on characterizing the NbO$_x$ deposits on the NbO$_x$-modified Pt catalyst and the adsorption and reaction of $m$-cresol on sites present on the NbO$_x$. 
4.3.3 Characterization of NbO\textsubscript{x} deposits on Pt(111)

XPS was used to characterize the NbO\textsubscript{x} films that were vapor-deposited onto the Pt(111) surface. Nb(3d) XPS spectra for (a) 0.5 ML, (b) 2.0 ML, and (c) 4.0 ML NbO\textsubscript{x} coverages are displayed in Figure 4.2. The spectrum in Figure 4.2(a) for the 0.5 ML NbO\textsubscript{x}-Pt(111) sample contains multiple overlapping peaks, which, as shown in the figure, can be curve resolved into two sets of 3d\textsubscript{3/2}, 3d\textsubscript{5/2} doublets, corresponding to Nb\textsuperscript{4+} (205.6 and 208.0 eV) and Nb\textsuperscript{5+} (207.2 and 209.6 eV) \[85,86\]. Based on the Gibbs free energies of formation for the various niobium oxides \[87\], for the oxygen annealing conditions used here (4×10\textsuperscript{-7} torr O\textsubscript{2}, 750 K), niobium should be in its fully oxidized form, \textit{i.e.} Nb\textsubscript{2}O\textsubscript{5}. This is clearly not the case, however, and based on the XPS peak areas it is estimated that the 0.5 ML oxide layer contains 66 % Nb\textsuperscript{4+} and only 34 % Nb\textsuperscript{5+}. As shown in the Figure 4.2 and by the tabulated values in Table 4.1, the niobium film becomes more oxidized with increasing thickness, and by 4 ML contains 83 % Nb\textsuperscript{5+} which more closely approaches that predicted by bulk thermodynamics. These data demonstrate that interactions at the Nb-Pt interface help stabilize the niobium film in a partially reduced form.
Figure 4.2 Nb(3d) XPS spectra for (a) 0.5 ML (b) 2.0 ML, and (c) 4.0 ML NbO\textsubscript{x} films on Pt(111).

<table>
<thead>
<tr>
<th>Coverage</th>
<th>Nb\textsuperscript{4+}</th>
<th>Nb\textsuperscript{5+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 ML NbO\textsubscript{x}/Pt(111)</td>
<td>66%*</td>
<td>34%</td>
</tr>
<tr>
<td>2.0 ML NbO\textsubscript{x}/Pt(111)</td>
<td>42%</td>
<td>58%</td>
</tr>
<tr>
<td>4.0 ML NbO\textsubscript{x}/Pt(111)</td>
<td>27%</td>
<td>83%</td>
</tr>
</tbody>
</table>

*The error in these values is estimated to be ±2%*

Table 4.1 Percentage of each niobium oxidation state for different NbO\textsubscript{x} coverages.
4.3.4 Temperature programmed desorption studies

TPD was used to provide insight into the adsorption and reaction of $m$-cresol on pristine Pt(111) and a Pt(111) surface that had been modified with 0.5 ML of vapor-deposited NbO$x$. TPD data obtained from the Pt(111) surface following exposure to 0.6 L of $m$-cresol at 150 K are displayed in Figure 4.3. Weakly bound unreacted $m$-cresol desorbs in a sharp peak centered at 245 K and the only reaction products detected were H$_2$ and CO. The H$_2$ desorption spectrum contains a broad peak at 350 K, a sharper peak at 535 K, and a broad low-intensity feature between 550 and 750 K. The peak at 350 K is characteristic of the recombinative desorption of H atoms from Pt(111) [62]. This peak indicates the presence of adsorbed H on the surface and demonstrates scission of either the O-H or some of the C-H bonds in the adsorbed $m$-cresol has occurred by this temperature.

The CO desorption spectrum contains a small peak centered at 460 K which is indicative of desorption limited CO from Pt(111) and may be due to the adsorption of a small amount of CO from the chamber background. The CO spectrum also contains a prominent peak at 535 K, and a much smaller peak at 600 K. The simultaneous desorption of H$_2$ and CO at 535 K indicates a reaction limited process which we assign to the unselective decomposition of $m$-cresol-derived species adsorbed on the surface. The higher temperature CO desorption features can be assigned to further decomposition of hydrocarbon fragments that remain on the surface. Note that these results are consistent with what we have reported previously for the reaction of $m$-cresol on Pt(111) [45].
Figure 4.3 TPD spectra obtained following exposure of the Pt(111) surface to 0.6 L of \textit{m}-cresol.

As shown by the \textit{m}-cresol TPD data in Figure 4.4, which was obtained from a 0.5 ML NbO\textsubscript{x}/Pt(111) sample, decorating the Pt(111) surface with NbO\textsubscript{x} significantly altered its reactivity toward \textit{m}-cresol. While the low-temperature molecular \textit{m}-cresol desorption feature is similar to that from Pt(111) and CO and H\textsubscript{2} were still the primary reaction products, the CO spectrum was now dominated by the low-temperature peak which we again believe is due to some CO adsorbing from the chamber background. Another important difference is that the H atom recombinative desorption peak at 350 K is almost absent for reaction on NbO\textsubscript{x}/Pt(111) compared to Pt(111). This indicates that the addition of the NbO\textsubscript{x} decreases or poisons the activity for C-H bond scission resulting in the adsorbed intermediate species being more stable on NbO\textsubscript{x}/Pt(111).

Another interesting feature in the \textit{m}-cresol TPD data from the NbO\textsubscript{x}/Pt(111) sample is the presence of a small H\textsubscript{2}O desorption peak at 480 K. Note that this product was not observed for Pt(111). In light of the high selectivity for the production of toluene from \textit{m}-cresol
obtained in the reactor studies with high surface area catalysts, we speculate that the H₂O product results from reaction between hydroxyl groups that are produced via C-O bond cleavage in the adsorbed m-cresol.

Figure 4.4 TPD spectra obtained following exposure of the NbOₓ/Pt(111) surface to 0.6 L of m-cresol.

We also used TPD to investigate the reaction of m-cresol on Pt(111) surface that was covered with 4 ML of NbOₓ (see Figure 4.5). This sample was unreactive toward m-cresol and the only desorbing specie detected was physisorbed m-cresol at 250 K. This is an important result since it demonstrates that Nb₂O₅ is not reactive toward m-cresol and that the partially reduced form of NbOₓ that is present in sub-monolayer films on Pt is required for selective HDO of m-cresol to produce toluene.
Figure 4.5 TPD spectra obtained following exposure of the 4.0ML-NbOx/Pt(111) surface to 0.6 L of m-cresol.

4.3.5 High resolution electron energy loss spectroscopy studies

HREELS was used to identify the structure and bonding configuration of m-cresol and m-cresol-derived intermediates on both Pt(111) and 0.5 ML NbOx/Pt(111) surfaces. Figure 4.6 shows HREELS spectra as a function of temperatures for Pt(111) dosed with 0.6 L m-cresol at 160 K. As noted above, the spectra corresponding to higher temperatures were obtained by briefly heating the sample to the indicated temperature and then letting it cool back to 160 K, at which point the spectrum was collected. In a previous study [45], we concluded based on HREELS data that m-cresol prefers to bond to the Pt(111) surface in a lay flat configuration in which the aromatic ring interacts strongly with the surface. This configuration would facilitate hydrogenation of the ring and is likely why the Pt/C catalyst produces a range of ring saturation products. We also observed that O-H scission in adsorbed m-cresol occurs at relatively low temperatures on Pt(111). While the reader is referred to our previous study for a detailed analysis of the m-cresol/Pt(111) HREELS data
that led to these conclusions, the most salient aspects of the analysis can be gleaned from the data in Figure 4.6.

The spectrum of adsorbed $m$-cresol at 160 K is consistent with the IR and Raman spectra of molecular $m$-cresol [63–65] with individual peak assignments given in Table 4.2. Upon increasing the temperature to 250 K, which is sufficient to desorb any physisorbed $m$-cresol species as demonstrated by the TPD results, small changes were observed including the disappearance of the broad $\nu$(O-H) mode between 3240 cm$^{-1}$ and 3580 cm$^{-1}$ and a decrease in the intensity of the $\nu$(C-H) peak of the aromatic ring at 3000 cm$^{-1}$. The former change indicates that scission of either the O-H bond or perhaps the C-O bond has occurred by this temperature, but the persistence of the $\nu$(C-O) mode at 1270 cm$^{-1}$, supports the former. The intensity of the $\nu$(C-H)$_{\text{ring}}$ peak of the aromatic ring at 3000 cm$^{-1}$ relative to that in 160 K spectrum suggests that the aromatic ring is positioned parallel to the surface for the adsorbed $m$-cresol species, since for this configuration the induced image dipoles in the metal would decrease the cross-section for exciting this mode. Heating to 300 K led to more significant changes in the HREEL spectrum, especially in the C-H bending region where there was a large diminution in the intensity of the out-of-plane bending mode at 785 cm$^{-1}$ and an increase in the intensity of the in-plane bending mode at 860 cm$^{-1}$. Based on this spectrum alone, we are not able to unambiguously identify the adsorbed species that are present on the surface at this temperature. It is clear, however, that decomposition of the adsorbed $m$-cresol has started to occur by this temperature, as signified by the decrease in the intensity of aromatic $\nu$(C-H)$_{\text{ring}}$ mode at 3000 cm$^{-1}$ relative to that of the $\nu$(C-H)$_{\text{methyl}}$ peak at 2950 cm$^{-1}$ and the appearance of peaks in the C-O stretching region of the bridge and atop peaks of adsorbed CO at 1750 and 2000 cm$^{-1}$. Further unselective
decomposition of the adsorbed intermediates were observed upon heating the sample to 350 K and above including bridge and atop $\nu$(C-O) peaks shifting up in energy to 1850 and 2100 cm$^{-1}$ respectively and the appearance of a prominent peak at 480 cm$^{-1}$ which can be attributed to the Pt-C stretching mode associated with carbon atoms or small hydrocarbon fragments adsorbed on the surface. These observations are consistent with the reaction-limited H$_2$ and CO desorption peaks between 500 and 560 K in the TPD data.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Frequency (cm$^{-1}$)</th>
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<tbody>
<tr>
<td></td>
<td>IR/Raman</td>
</tr>
<tr>
<td>$\gamma$(C-H)$_{\text{ring}}$ (in plane mode)</td>
<td>700</td>
</tr>
<tr>
<td>$\gamma$(C-H)$_{\text{ring}}$ (Out of plane mode)</td>
<td>739</td>
</tr>
<tr>
<td>$\nu$(C-O) (C-O stretching)</td>
<td>1260</td>
</tr>
<tr>
<td>$\delta_{\text{CH}_2}$ (symmetric)</td>
<td>1365</td>
</tr>
<tr>
<td>$\delta_{\text{CH}_2}$ (asymmetric)</td>
<td>1425</td>
</tr>
<tr>
<td>$\nu$(C-H)$_{\text{methyl}}$</td>
<td>2924</td>
</tr>
<tr>
<td>$\nu$(C-H)$_{\text{ring}}$</td>
<td>3042</td>
</tr>
<tr>
<td>$\nu$(O-H)</td>
<td>3240</td>
</tr>
</tbody>
</table>

$s$-symmetric, $as$-asymmetric, $b$-bend, $v$-stretch, $\delta$-deformation, $p$-rock, $\gamma$-wag, $\chi$-scissor.

**Table 4.2.** Vibrational modes assignments of $m$-cresol on Pt(111) and NbO$_x$/Pt(111) surface.
Figure 4.6 HREEL vibrational spectra as a function of temperature for Pt(111) dosed with 0.6 L \textit{m}-cresol at 160 K.

Similar to our previous studies for WO\textsubscript{x}-decorated Pt(111) surfaces \cite{88, 89}, the addition of NbO\textsubscript{x} to Pt(111) significantly changed the adsorption and reaction of \textit{m}-cresol as shown by the HREELS spectra as a function of temperature for a 0.5 ML NbO\textsubscript{x}-Pt(111) sample saturated with 0.6 L \textit{m}-cresol displayed in Figure 4.7. The spectrum at 160 K is similar to that of \textit{m}-cresol adsorbed on Pt(111) at this temperature and is also consistent with the IR and Raman spectra for \textit{m}-cresol \cite{63–65}. Increasing the temperature from 160 K to 250 K to desorb the weakly bound physisorbed species produced only minor changes including the diminution of the intensity of the $\gamma$(C-H) mode at 700 cm$^{-1}$ and an increase in the intensity of the symmetric $\delta$CH$_3$ mode at 1410 cm$^{-1}$ relative to that of asymmetric $\delta$CH$_3$. 

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mode at 1470 cm\textsuperscript{-1}. Since it is unlikely that reaction has occur at such a low temperature, this change must be due to the orientation of the chemisorbed species at 250 K relative to the more randomly orientated molecules in the condensed physisorbed layer at 160 K. It has previously been shown in studies of alkanethiols on metal surfaces that the methyl group symmetric vibrational mode becomes more intense relative to the asymmetric vibrational mode as the methyl group becomes oriented closer to the surface normal\cite{75}. Based on this observation, the relative intensities of the asymmetric and asymmetric $\delta_{\text{CH}_3}$ modes obtained here indicate that the methyl group is oriented away from the surface. This would require a similar configuration for the aromatic ring. This conclusion that on the NbO$_x$/Pt(111) surface \textit{m}-cresol bonds in an upright configuration with the ring tilted away from the surface is further supported by the strong intensity of the $\nu$(C-H)$_{\text{ring}}$ peaks at 3000 cm\textsuperscript{-1}. If the ring were lying flat on the surface the induced dipole in the metal would screen the $\nu$(C-H)$_{\text{ring}}$ modes leading to low intensity for these peaks as is observed on the Pt(111) surface (see Figure 4.6). Small $\nu$(C-O) peaks at 1780 cm\textsuperscript{-1} and 2030 cm\textsuperscript{-1} due CO adsorbed on bridging and atop sites on bare portions of the Pt(111) surface are also apparent in the spectrum at 250 K. Based on comparison to blank experiments we conclude that these peaks result from the adsorption of CO form the background gas in the vacuum chamber. This artifact is unfortunately unavoidable due to the time it takes to collect the HREEL spectra.

Heating the surface to 300 K caused the $\nu$(C-O) mode at 1260 cm\textsuperscript{-1} to disappear while the $\nu$(O-H) peak between 3100 cm\textsuperscript{-1} and 3600 cm\textsuperscript{-1}, which is broadened due to hydrogen bonding in the physisorbed layer, is replaced with a more distinct $\nu$(O-H) peak at 3340 cm\textsuperscript{-1}. These changes indicate that scission of the C-O bond may have occurred at least for a
portion of the adsorbed species with the hydroxyl group remaining on the surface. At the same time, the relative intensity of ν(C-H)_{methyl} mode at 2950 cm\(^{-1}\) and ν(C-H)_{ring} mode at 3000 cm\(^{-1}\) remain unchanged which suggests that the aromatic ring still remains intact. Unfortunately, several reaction intermediates are likely on the surface at this temperature, so it is not possible to assign the spectrum of the m-cresol-dosed NbO\(_x\)/Pt(111) at 300 K to specific adsorbed species.

Upon further increasing the temperature to 350 K and higher, various changes were observed including the disappearance of ν(O-H) stretching mode near 3340 cm\(^{-1}\), an increase in the intensity of the ν(C-H)_{ring} mode relative to that of the ν(C-H)_{ring} mode, and an increase in the intensity of C-O stretching mode at 1830 cm\(^{-1}\) and 2080 cm\(^{-1}\). These changes suggest that unselective decomposition of the adsorbed intermediates has started to occur by this temperature.
Figure 4.7 HREEL vibrational spectra as a function of temperature for 0.5 ML NbO$_x$-Pt(111) dosed with 0.6 L m-cresol at 160 K.

4.4 Discussion

As demonstrated by the kinetics data obtained in this study for the reaction of m-cresol on Pt/C, group-10 based catalysts can exhibit reasonably high selectivity to aromatic hydrocarbons during HDO of aromatic oxygenates. As noted in the introduction, however, these metals also tend to produce a significant number of products in which the aromatic ring has been saturated. In the case of m-cresol these include methylcyclohexanol, methylcyclohexanone, and methylcyclohexane (see Figure 4.1). This and similar observations in previous studies have led to the conclusion that for m-cresol the reaction pathway proceeds through the initial hydrogenation of the ring to produce the keto-enol
tautomerization pair, methylcyclohexanol and methylcyclohexanone, with further hydrogenation and/or dehydrogenation of these species producing methylcyclohexane and toluene [42,79,89,90]. This so-call tautomerization pathway is shown schematically in Figure 4.8a. Direct hydrogenolysis of the C-O bond in m-cresol could also occur in a single step to produce toluene as shown in Figure 4.8b. The observed product selectivity for the Pt/C catalyst, including the relatively high selectivity to toluene, suggests that on this catalyst both of these pathways may occur to an appreciable extent.

In contrast, the 95% selectivity to toluene during HDO of m-cresol when using NbOₓ-Pt/C strongly suggests that for this catalyst the reaction proceeds exclusively via the direct deoxygenation pathway. The small amount of methylcyclohexane produced can be attributed to hydrogenation of a portion of the toluene product on bare Pt. It is noteworthy that this catalyst also exhibited higher overall activity than Pt/C. As noted above, these results are similar to what we reported previously for the HDO of m-cresol over WOₓ-Pt/C[42,45] and that reported by Guo et al.[43] for Nb2O5-Ru/SiO2. Clearly for these systems the oxide surface modifier, WOₓ or NbOₓ, greatly enhances the preference for the direct deoxygenation pathway. For the WOₓ-Pt system we previously concluded that the catalyst was bifunctional where the Pt provides activity for H₂ dissociation while the WOₓ provides adsorption sites for the m-cresol which interacts via the hydroxyl oxygen with under-coordinated W cations. We note that a similar mechanism has also been proposed by Hong et al. for the HDO of m-cresol over Pd/Fe₂O₃ [91]. In that study the Fe₂O₃ was the support rather than a surface modifier on the Pd. Nonetheless, they concluded that the Pd facilitated partial reduction of nearby Fe₂O₃ under an H₂ atmosphere via dissociation of the H₂ on Pd and the spillover of H atoms onto the Fe₂O₃. The oxygen vacancies in the
FeO$_x$ were again thought to be sites for $m$-cresol adsorption and reaction. The XPS results obtain here for NbO$_x$-Pt(111) in UHV (i.e. in the absence of H$_2$) demonstrate, however, that H spillover is not needed to maintain the NbO$_x$ in a partially reduced state and that interactions at the NbO$_x$-Pt interface are sufficient for this purpose. While this result is consistent with what we reported previously for WO$_x$-Pt(111), the results obtained here provide a much more definitive demonstration of the stabilization of the suboxide via interactions with the underlying Pt. This is clearly demonstrated by the XPS results in Figure 4.2 which show that for the same oxidizing conditions, a 4 ML NbO$_x$ film on Pt(111) is nearly fully oxidized, while a 0.5 ML film remains highly reduced. It is also noteworthy that while interactions between Pt and each oxide helped maintain them in partially reduced states, this effect was more pronounced for niobium compared to tungsten resulting in a higher extent of reduction for an equivalently thick film.

![Proposed pathways for HDO of aromatic oxygenates over various catalysts.](image)

**Figure 4.8** Proposed pathways for HDO of aromatic oxygenates over various catalysts.

The results obtained here for Pt(111) and NbO$_x$/Pt(111) also provide additional insight into the adsorption sites and adsorbed species involved in the reaction of $m$-cresol on these
catalysts. The nearly fully oxidized Nb$_2$O$_5$ multilayer was inactive toward $m$-cresol with only weakly adsorbed species being observed by TPD. In contrast, $m$-cresol adsorbed strongly on both Pt(111) and 0.5 ML NbO$_x$/Pt(111) but reacted to form distinct species on the two surfaces. On Pt(111) there is a strong ring-surface interaction and the HREELS spectrum of $m$-cresol adsorbed on Pt(111) indicates that the aromatic ring is oriented parallel to the surface. This result is consistent with the DFT calculation by Tan et al.[71] which predict that $m$-cresol adsors in a lay-flat geometry on bridge sites on Pt(111) with bonding via the aromatic ring carbons. Our HREELS results also show that on Pt(111) under UHV conditions decomposition of the aromatic ring commences near 300 K.

In contrast to Pt(111), the HREELS data for $m$-cresol-dosed 0.5 ML NbO$_x$-Pt(111) demonstrate that the adsorption geometry is one in which the aromatic ring is tilted away from the surface, a bonding configuration that under steady state reaction conditions would be expected to suppress both ring hydrogenation and ring opening [92]. The HREELS data also indicate that scission of the C-O bond in this adsorbed species is facile and occurs below 300 K with the resulting toluenic intermediate being relatively stable and remaining intact up to 300 K. With the data obtained in the present study we are not able to determine the adsorption site for this species but speculate that it must be on the Pt(111) surface since the C-O scission reaction would saturate the cation site on the NbO$_x$ with hydroxyl groups. Based on these results we therefore propose the reaction pathway shown schematically in Figure 4.9 for the reaction of $m$-cresol on NbO$_x$-decorated Pt(111). Under UHV conditions the adsorbed toluenic intermediate ultimately decomposes, but under typical HDO reaction conditions where the Pt surface would be saturated with H atoms, this species could easily combine with an H atom to form gaseous toluene.
Figure 4.9 Proposed pathways and intermediates for the adsorption and reaction of \textit{m}-cresol on NbO$_x$/Pt(111).

4.5 Conclusions

The results of this study demonstrate that NbO$_x$-Pt/C is a highly selective catalyst for the HDO of \textit{m}-cresol to produce toluene. The high selectivity to toluene (>95\%) and the lack of a significant production of keto-enol and ring hydrogenation products indicate that the reaction proceeds via direct hydrogenolysis of the C-O bond rather than by the tautomerization pathway that has been proposed for unmodified Pt catalysts. The model catalyst studies demonstrated that interaction at the NbO$_x$-Pt interface helps stabilize the NbO$_x$ in a partially reduced state which contains undercoordinated Nb cations that provide bonding sites for the hydroxyl oxygen in \textit{m}-cresol. Adsorption on these sites produces a bonding configuration in which the aromatic ring is tilted away from the surface. This is in contrast to pure Pt surfaces in which there is a strong surface-ring interaction resulting in a lay-flat adsorption geometry which facilitates ring hydrogenation.
Chapter 5 WO$_x$ promoted Nickel Catalyst for Hydrodeoxygenation

$m$-Cresol

Summary

The effect of decorating the surface of a Ni catalyst with WO$_x$ on its activity and selectivity for the hydrodeoxygenation (HDO) $m$-cresol was investigated. The reaction of $m$-cresol in the presence of H$_2$ over an unmodified Ni/C catalyst produced both toluene and methylocyclohexane as well as a range of products in which the ring had been hydrogenated. This catalyst was also active for C-C bond hydrogenolysis at temperatures above 600 K. In contrast, modifying the Ni with a sub-monolayer amount of WO$_x$ deposited via atomic layer deposition (ALD) enhanced the $m$-cresol HDO selectivity with toluene and methylocyclohexane being the only products produced indicating that the reaction proceeds via direct pathway on this catalyst. XPS in this and previous studies indicate that synergistic
interactions between the WO$_x$ and the Ni help maintain a high concentration of oxygen vacancies in the monolayer WO$_x$ species which are the active sites for the HDO reaction.

5.1 Introduction

Lignocellulosic biomass, as a promising feedstock for carbon-based fuels and chemicals, has attracted much research effort aimed at developing efficient catalytic pathways for the upgrading of the constituent molecules in biomass into more useful products [5–7,10–13]. While much of this work initially focused on the cellulosic fraction of biomass, the possibility of producing high-value aromatic molecules from lignin has recently motivated studies of the upgrading of this component of biomass. Depolymerization of lignin via fast pyrolysis or other means produces a range of unstable, immiscible and highly polar aromatic compounds with a high oxygen content [14,15]. Removal of at least a portion of the oxygen-containing functional groups is therefore an important step in the upgrading of lignin-derived molecules and has motivated the
development of highly active and selective hydrodeoxygenation (HDO) catalysts for this purpose.

Early studies in this area focused on using supported noble metals, including Pt, Pd and Ru [20–23], and less expensive supported base metal catalysts, such as Fe and Ni [26–28], for selective C-O bond hydrogenolysis in oxygenated aromatics, including guaiacol, cresol and phenol, that are produced during depolymerization of lignin. Although all of these systems were found to have some activity for the desired HDO reactions, they tended to also catalyze hydrogenation of the aromatic rings leading to lower value products and suffered from rapid deactivation due to coking. Alloying group 10 metals with a second more oxyphilic metal, such as Fe, Zn, Mo, has been shown to enhance the selectivity to the desired aromatic products [88,89,93], although further improvements in selectivity are still needed. Recently, we and others have demonstrated that bifunctional catalysts consisting of a supported group 10 metal decorated with a reducible oxide, e.g. WO$_x$-Pt/C, NbO$_x$-Pt/C, exhibit high activity and selectivity for HDO of oxygenated aromatics [42,43,46]. For example, in a study of the HDO of $m$-cresol over WO$_x$-modified Pt supported on carbon we observed a selectivity to toluene in excess of 98% for reaction at 623 K [42]. Another interesting aspect of these bifunctional catalysts is that the HDO reaction appears to proceed via a direct C-O bond hydrogenolysis pathway [90,94,95] (see Figure 5.1) which is in contrast to the unmodified metals where HDO involves the initial hydrogenation of the aromatic rings to produce a tautomerization pair, followed by dehydration to remove the oxygen-containing functional groups [79,96,97]. This pathway tends to be less selective and produces a range of aromatic and nonaromatic products.
Figure 5.1 Proposed pathways for HDO of aromatic oxygenates.

In the work reported here, we have expanded our previous studies of WO$_x$- and NbO$_x$-modified Pt catalysts to the analogous WO$_x$-modified Ni catalyst in order to explore whether high HDO selectivity can be obtained using this less expensive metal. The reactions of $m$-cresol on high surface area WO$_x$-Ni/C catalysts in the presence of H$_2$ were measured using an atmospheric pressure flow reactor. Atomic Layer Deposition (ALD) was used to control the amount of WO$_x$ added to the catalyst and allowed us to explore how both the coverage and thickness of the oxide modifier affected catalytic properties. XPS studies using model Ni foil catalysts were also carried out and provide insight into interactions at the Ni-WO$_x$ interface.

5.2 Experimental

A 5 wt% Ni/C catalyst was prepared using the incipient wetness technique. The nickel(II)-nitrate hexahydrate precursor (98%, Alfa Aesar) was dissolved in a water/ethanol (3:1) mixture and then activated carbon (1000 m$^2$/g, Strem) was added to the solution under continuous stirring. The resulting slurry was dried in an oven at 333 K for
12 h and reduced at 773 K in a continuous flow reactor with 5% H₂ in a 60 mL/min He carrier gas. ALD was used to modify the Ni/C surface with WOₓ and to produce a WOₓ/C catalyst. The ALD was performed using a custom-built vacuum deposition system that has previously been described in detail [53]. Each ALD deposition cycle consisted of exposing the Ni/C catalyst, held at 473 K, to a tungsten hexacarbonyl precursor (W(CO)₆, 99%, Strem) for 3 min, followed by evacuation using a mechanical vacuum pump for 3 mins to remove weakly adsorbed species. The sample was then exposed to excess air at 473 K for 6 mins to oxidize the adsorbed W(CO)₆ precursor. After finishing all ALD deposition cycles, the sample was heated in air at 673 K for 1 min to completely oxidize the WOₓ layer. The amount of tungsten oxide deposited in each ALD cycle was measured gravimetrically. Figure 5.2 displays a plot of the WO₃ wt% loading as a function of the number of WOₓ ALD cycles for the Ni/C catalyst. As shown in this plot, a single WOₓ ALD cycle produced a catalyst with 3.6 wt% WO₃. XRF analysis (Epsilon 1, Malvern Panalytical) was also used to confirm overall catalyst compositions.

Scanning transmission electron microscopy (STEM) and Energy Dispersive X-ray Spectroscopy (EDS) were used to characterize the structure of the catalysts and were conducted using a JEOL JEM-F200 STEM operated at 200 kV. The samples for the STEM/EDS analysis were prepared by suspending the powder catalyst in ethanol and then depositing onto a lacey carbon film (Electron Microscopy Sciences, USA).
Figure 5.2 WO$_3$ loading as a function of the number of ALD cycles on a 5 wt% Ni/C surface.

X-ray photoelectron spectroscopy (XPS) was used to characterize how interactions at the WO$_x$-Ni interface affect the WO$_x$ layer. These studies used a Ni foil as the substrate with the WO$_x$ being added via a single ALD cycle identical to that described above. To ensure the surface of the Ni foil was completely reduced prior to ALD, it was initially subjected to a 2 h reduction treatment at 773 K in a continuous flow reactor with 5% H$_2$ in a 60 mL/min He carrier gas. After ALD the foil (1R-WO$_x$-Ni) was attached to the sample holder on the UHV system that housed the XP spectrometer and evacuated to a pressure of $\sim$1 x 10$^{-9}$ torr. XP spectra were collected using a hemispherical electron energy analyzer (Leybold-Heraeus) with an Al K$\alpha$ X-ray source (VG Microtech). The binding energy scale of XPS spectra was referred to the adventitious C(1s) peak, which was assumed to be located at 284.8 eV.
5.3 Results

![Figure 5.2 HAADF-STEM images and EDS elemental mapping of 2R-WO\textsubscript{x}-NiC.](image)

STEM and EDS mapping were used to characterize the structure of a 5 wt% Ni/C catalyst that had been modified with two WO\textsubscript{x} ALD cycles which produced a 7.2 wt% loading of WO\textsubscript{3}. An HAADF-STEM image of this sample along with EDS maps for Ni and W from the indicated region are displayed in Figure 5.3. Note that the catalyst contains relatively large Ni particles that range in size from 5 to 25 nm. Comparison of the Ni and W EDS maps reveals that the WO\textsubscript{x} was preferentially deposited on the surface of the Ni particles with the exposed potions of the C support being largely devoid of tungsten.

XPS was used to further characterize the submonolayer WO\textsubscript{x} deposits on the Ni surface (Figure 3). In this experiment a Ni foil was subjected to a single WO\textsubscript{x} ALD cycle using the same procedure as that used for the supported Ni catalyst. Note that the last step of the ALD cycle was to anneal the sample in air at 673 K, a condition which should result in complete oxidation of the tungsten; thus, one would expect the W(4f) spectrum to contain only peaks indicative of W\textsuperscript{6+}. As shown in Figure 5.4, the XPS spectrum contains a doublet with peaks centered at 36.0 eV and 38.1 eV which are the expected positions for
the W(4f_{7/2}) and W(4f_{5/2}) peaks for W^{6+} [98–100]; however, a smaller W(4f_{7/2})-W(4f_{5/2}) doublet with peaks centered at 34.8 eV and 37.0 eV which are consistent with W^{5+} can also be resolved. Thus, it appears that at least in the submonolayer regime, the Ni-supported WO_x contains a high concentration of oxygen vacancies.

![Figure 5.4 W(4f) XPS spectra for Ni foil decorated with 1 WO_x ALD deposition cycle.](image)

Figure 5.4 W(4f) XPS spectra for Ni foil decorated with 1 WO_x ALD deposition cycle.

The HDO of m-cresol on 5 wt% Ni/C catalysts was studied as a function of both the weight loading of the WO_x modifier and temperature. The conversion and product selectivity for an unmodified Ni/C and one modified with 7.2 wt% of WO_x (2 ALD deposition cycles) at 523 K are displayed in Figure 5.5. In these experiments the reactant stream was at a total pressure of 1 bar with a H_2 to m-cresol ratio of 10 to 1 and a weight hourly space velocity (WHSV) of 1 h^{-1} with the data being collected after about 30 minutes on stream. Blank studies using just the carbon support that had been subjected to 2 WO_x ALD cycles were also performed, and this catalyst was found to be inactive. The data for Ni/C show that while it was very active and produced a m-cresol conversion of 86%, it had
a low selectivity of only 8.6% for the desired HDO aromatic product, toluene. The primary products for this catalyst were methylcyclohexanol (MCH, 31.1%), methylcyclohexanone (ONE, 38.2%) and methylcyclohexane (MCH, 21.9%). Note that the ring has been saturated in all of these products consistent with the high hydrogenation activity of Ni. This catalyst was also found to be relatively stable under these conditions with the conversion decreasing by less than 10% after seven hours on stream (see Figure 5.6a) with little change in the product selectivity.

Decorating the surface of the catalyst with WO$_x$ significantly altered both activity and selectivity. For this catalyst the conversion was only 42% after 30 minutes on stream, but it exhibited 74.9% selectivity to the HDO product, methylcyclohexane, with the balance being the more desirable toluene product (25.0%). It should be noted that the nearly 3:1 methylcyclohexane to toluene product ratio for this catalyst is consistent with the expected equilibrium conversion for the hydrogenation of toluene to methylcyclohexane at 523 K. The WO$_x$-Ni/C was less stable, however, than the Ni/C with the overall conversion decreasing by 25% after seven hours on stream (see Figure 5.6a) with the product selectivity remaining nearly constant. As will be discussed below, the disparity in the range of products produced from the Ni/C and WO$_x$-Ni/C indicates that different reaction pathways occur on the two catalysts.
Figure 5.5 Conversion and selectivity for HDO of \textit{m}-cresol over Ni/C and 2R-WO\textsubscript{x}-Ni/C catalysts. Reaction conditions: temperature of 523 K, total pressure of 1 bar, \textit{H}_2/\textit{m}-cresol \textasciitilde10 and WHSV of 1 h\textsuperscript{-1}.

Figure 5.6 Time-on-stream experiments for HDO reaction of \textit{m}-cresol over Ni/C and WO\textsubscript{x}-Ni/C at (a) 523 K and (b) 623 K. Reaction conditions: Reaction conditions: total pressure of 1 bar, \textit{H}_2/\textit{m}-cresol \textasciitilde10 and WHSV of 1 h\textsuperscript{-1}. Conversion (black), yields of TOL (red) and yields of MCH (blue).
Figure 5.7 displays similar data for reaction of \( m \)-cresol on WO\(_x\)-Ni/C and Ni/C catalysts at 623 K for the aforementioned reaction conditions. It is interesting that at this temperature the Ni/C catalyst exhibited a relatively high selectivity of 72.7\% to toluene with much smaller amounts of methane (15.4\%), phenol (7.7\%), methylcyclohexane (3.1\%) and methylcyclohexanone (1.1\%) also being produced. The methane and phenol products demonstrate that C-C bond hydrogenolysis occurs to an appreciable extent at this temperature. Somewhat surprisingly, while being much more selective for the desired HDO pathway at 623 K, the Ni/C catalyst was significantly less active at this temperature than at 523 K achieving a conversion of only 35\% after 30 minutes on stream and decreasing to 25\% after seven hours on stream (see Figure 5.6b). The fact that the amount of methane produced was greater than the amount of phenol indicates that some unselective decomposition of the \( m \)-cresol is likely taking place which could result in coking of the Ni surface and account for the more rapid deactivation at the higher temperature.

As would be expected, upon increasing the temperature to 623 K the activity of the WO\(_x\)-modified Ni/C catalyst increased obtaining a conversion of 70.6\% after 30 minutes on stream which is two-fold higher than that of the unmodified Ni/C catalyst. It also remained highly selective for HDO of \( m \)-cresol and exhibited 89.0\% and 7.3\% selectivity to toluene and methylcyclohexane, respectively. The only other products were small amounts of phenol (0.1\%) and methane (2.5\%) which may have been produced via C-C bond hydrogenolysis on bare portions of the Ni. Like Ni/C, the WO\(_x\)-modified catalyst was not very stable for these reaction conditions and the overall conversion dropped to only 20\% after seven hours on stream (Figure 5.6b).
As noted above, the large discrepancy in the conversion and selectivity for Ni/C and WO\textsubscript{x}-Ni/C at 523 K suggests different reaction pathways occur on the two catalysts. To provide additional insight into this, reactivity studies were also carried out using methylcyclohexanone as the reactant. This molecule was chosen because it is one of the intermediates in the \textit{m}-cresol tautomerization HDO pathway that has been proposed in the literature for supported metal catalysts [20,21,101]. Conversion and selectivity data for reaction at 523 K and a WHSV of 1 h\textsuperscript{-1} for the Ni/C and 7.2 wt % WO\textsubscript{x}-Ni/C catalysts are shown in Figure 5.8. For comparison, analogous data for reaction of \textit{m}-cresol on the two catalysts are also included in this figure (these data were again collected after 30 minutes on stream). Note that the products are grouped according to hydrocarbons (HC) that consist of toluene (TOL) and methylcyclohexane (MCH) and oxygen-containing hydrocarbons that consist of methylcyclohexanone (ONE), methylcyclohexanol (OL), and cresol.
For the WO₃-Ni/C catalyst the conversion was much higher for the methylcyclohexanone reactant, nearly 100 %, compared to only 42 % for m-cresol, but the product slates were similar with methylcyclohexane and toluene being the only products in a ratio close to that for equilibrium being established for their interconversion (\(i.e.\) 
\[C₆H₁₁CH₃ + 3 H₂ \leftrightarrow C₆H₅CH₃\). This is consistent with the reaction proceeding via direct C-O bond hydrogenolysis for both reactants followed by hydrogenation/dehydrogenation to achieve the equilibrium product composition. For the Ni/C catalyst the overall conversion was comparable for the two reactants but there were differences in the range of products produced, including higher selectivity to the methylcyclohexane and toluene HDO products and the appearance of cresol as a product when methylcyclohexanone was used as the reactant. These results again indicate that the reaction pathways are much more complex on the Ni-only catalyst. While the possibility that some direct C-O bond hydrogenolysis may have occurred cannot be ruled out, the production of cresol as a product provides support for the tautomerization pathway shown in Figure 5.1.
Figure 5.8 Atmospheric HDO reaction of (a) $m$-cresol and (b) ONE over 2R-WO$_x$-Ni/C and Ni/C catalysts. Products are grouped as hydrocarbons (HC) and oxygen-containing hydrocarbons (O-HC). Reaction conditions: temperature of 523 K, total pressure of 1 bar, H$_2/m$-cresol $\sim$ 10 and WHSV of 1 h$^{-1}$.

The results presented above along with the observation that WO$_x$ by itself is not reactive toward $m$-cresol [42] suggest that the WO$_x$-Ni/C catalyst is either bifunctional or that synergistic interactions between the Ni and WO$_x$ are needed to produce catalytic sites on the WO$_x$ that have high activity for C-O bond hydrogenolysis. To study the relative importance of these effects, we investigated the activity and selectivity of WO$_x$-Ni/C catalysts for the HDO of $m$-cresol as a function of the WO$_x$ weight loading. These reactivity data were obtained using the same reaction conditions as those described above (collected after 30 minutes on stream) and are displayed in Figure 5.9. Parts (a) and (b) of the figure correspond to reaction at 523 K and 623 K, respectively. The number of ALD cycles required to achieve the WO$_x$ weight loading for each catalyst is given in Figure 5.2.
The data for reaction at 523 K shows that the overall conversion of \textit{m}-cresol on the WO\textsubscript{x}-Ni/C catalyst decreased with increasing WO\textsubscript{x} weight loading becoming nearly inactive for a WO\textsubscript{x} weight loading of 37.8\% which is sufficiently high to coat the Ni with multilayers of the oxide. This loss of activity at high WO\textsubscript{x} loadings is consistent with the WO\textsubscript{x}, by itself, being unreactive toward \textit{m}-cresol. The product trends with increasing WO\textsubscript{x} weight loading are quite interesting, however, with the yield and selectivity for methylcyclohexane going through a maximum at 7.2 wt\% WO\textsubscript{x}. For reaction at 623 K both the conversion and selectivity to toluene also go through a maximum at 7.2 wt\% WO\textsubscript{x}. Note that this WO\textsubscript{x} loading corresponds to 2 ALD cycles and, as will be discussed below, corresponds to less than monolayer coverage of WO\textsubscript{x} on the Ni surface. Thus, the sites that are active for C-O bond hydrogenolysis appear to be associated with this sub-monolayer phase of WO\textsubscript{x}.

\textbf{Figure 5.9} Conversion and yields for HDO of \textit{m}-cresol at (a) 523 K and (b) 623 K as function of the number of WO\textsubscript{x} ALD deposition cycles. Reaction conditions: total pressure of 1 bar, H\textsubscript{2}/\textit{m}-cresol \~ 10 and WHSV of 1 h\textsuperscript{-1}.  

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5.4 Discussion

In this study we observed that a Ni/C catalyst exhibits low selectivity for the HDO of \( m \)-cresol to produce toluene and methylcyclohexane at 523 K. Higher selectivity to the desired toluene product (72.7 \%) was obtained at 623 K, but C-C bond hydrogenolysis activity was also observed at this temperature. These results are consistent with previous studies in the literature of HDO of \( m \)-cresol over supported Ni catalysts [96,102–104]. For example, Yang et al. found that at atmospheric pressure, the gas-phase HDO of \( m \)-cresol on 5 wt% Ni/SiO\(_2\) primarily produced methycyclohexanone and methylcyclohexanol at 523 K and demethylation and cracking products, phenol and methane, at 623 K [102]. As noted in the introduction, the former slate of products has typically been ascribed to a reaction pathway that involves complete or partial hydrogenation of the aromatic ring in \( m \)-cresol to produces an intermediate pool containing these species [79,96,97]. The penchant for hydrogenating the aromatic rings at 523 K likely results from the strong interaction of the rings with Ni which tend to bind in a lay-flat geometry on this surface [96]. Deoxygenation products can be formed by this pathway through dehydration of some of these intermediates, as was observed in the present study for reaction of \( m \)-cresol on Ni/C at 623 K; however, at this higher temperature C-C bond hydrogenolysis is also significant which decreases the selectivity to the desired toluene HDO product [105].

Modification of the Ni/C with small amounts of WO\(_x\) was found to significantly alter HDO reactivity toward \( m \)-cresol with the selectivity to toluene plus methylcyclohexane approaching 100\% at 523 K, and a selectivity to toluene alone of 89\% at 623 K for a 7.2 wt % WO\(_x\)-Ni/C catalyst. The lack of production of methycyclohexanone, methylcyclohexanol, methane, and phenol for this catalyst along
with the results obtained when methycyclohexanone was used as the reactant both indicate that for the WO$_x$-modified catalysts HDO of $m$-cresol proceeds via direct C-O bond hydrogenolysis and does not require the production of an intermediate pool in which the aromatic ring has been hydrogenated. The high amount of methylcacylyhexane from WO$_x$-Ni/C at 523 K can be attributed to a sequential pathway in which toluene is initially produced and then hydrogenated to form the saturated product. This is also consistent with the production of an equilibrium toluene-methylcacylyhexane mixture at this temperature.

While WO$_x$-Ni/C exhibits interesting properties, the state of the WO$_x$ in the catalyst appears to play an important role in obtaining high HDO selectivity. This is demonstrated by the data in Figure 5.9 which show that high activity and selectivity are only obtained for catalysts with relatively low (<10%) weight loadings of WO$_x$. At higher weight loadings where the Ni is presumably covered with a thick layer of the oxide, the catalyst is essentially inactive, so the observed HDO activity cannot be ascribed to reaction on bulk WO$_3$. Rather, it appears that partially coating the Ni with WO$_x$ is required to obtain a highly selective catalyst. In a previous surface science study we examined the growth of WO$_3$ films on Pt(111) using ALD cycles similar to those used here except that they were done with the sample in an ultrahigh vacuum system which allowed XPS and TPD to be used to characterize the surface. In that study, CO TPD was used to show that each ALD cycle (using the W(CO)$_6$ precursor) resulted in a WO$_x$ coverage of ~0.4 monolayers. Assuming that the WO$_x$ growth rate on Ni is similar to that on Pt, the most selective WO$_x$-Ni/C catalyst (7.2% wt WO$_3$ or 2 ALD cycles) was coated with a sub-monolayer amount of WO$_x$. Furthermore, XPS results in our previous study of WO$_x$/Pt(111) show that in the sub-monolayer regime, interactions between the Pt and WO$_x$ help maintain the oxide in a
highly-reduced state that contains a mixture of $W^{+4}$, $W^{+5}$, and $W^{+6}$. While the XPS results for WO$_x$-Ni/C obtained in the present study using high surface area powder catalysts provide less definitive evidence for this, they still show that the Ni-supported tungsten oxide remains at least partially reduced under conditions for which completely oxidized WO$_3$ is the thermodynamically stable state.

The reactivity results obtained here are also similar to those reported previously by Wang et al. for HDO of $m$-cresol over WO$_x$-Pt/C catalysts [42]. In both cases HDO of $m$-cresol to produce toluene appears to occur via direct C-O bond hydrogenolysis and interactions of the oxide modifier with the metal surface helps stabilize the WO$_x$ in a partially-reduced state. DFT calculations for the WO$_x$-Pt system indicate that the phenolic oxygen in $m$-cresol binds with under-coordinated tungsten ions in the WO$_x$ surface complex and that these are the active sites for C-O bond cleavage [42]. This binding configuration also prevents direct interaction of the aromatic rings with the metal surface thereby hindering both ring hydrogenation and C-C bond hydrogenolysis. In addition to helping maintain the active sites on the WO$_x$, Ni or Pt have the important role of providing sites for facile dissociation of H$_2$ thereby providing the H atoms needed for the HDO reaction.

Finally, it should be noted that WO$_3$ is not the only reducible oxide modifier that can significantly enhance the selectivity for the HDO of $m$-cresol when using a supported metal catalyst. For example, in a study of Ni/SiO$_2$ catalysts Yang et al. reported that decorating the Ni particles with small amounts of MoO$_x$ produced a catalyst that was highly selective for the HDO of $m$-cresol to toluene under reaction conditions similar to those used
here [102]. They also concluded that oxygen vacancies in the MoO₃ were the active sites for the reaction. Similarly, we have recently reported on the HDO activity of a Pt/C catalyst in which the Pt was decorated with a sub-monolayer amount of NbOₓ using ALD [46]. This catalyst exhibited properties similar to that reported here for WOₓ-Ni/C including the interaction between the Pt and niobia helping to maintain the oxide in a partially reduced state. For reaction conditions similar to those used here, the NbOₓ-Pt/C catalyst exhibited 95 % selectivity to toluene for the HDO of m-cresol at 623 K.

5.5 Conclusions

In this study it was observed that WOₓ-modified Ni/C catalysts are highly activity and selective for the HDO of m-cresol to produce toluene and methycyclohexane. On the unpromoted Ni/C catalyst the HDO reaction proceeded via an indirect tautomerization pathway that produced significant amounts of methycyclohexanone and methycyclohexanol in addition to toluene and methycyclohexane. This catalyst also promoted hydrogenolysis of C-C bonds at higher temperatures. Decorating the surface of the Ni with WOₓ significantly enhanced HDO selectivity to toluene and methycyclohexane and inhibited the activity for ring hydrogenation and C-C hydrogenolysis. At 623 K this catalyst achieved 89% selectivity to the desired toluene product. The lack of products with hydrogenated rings for this catalyst indicates that the reaction follows a direct HDO pathway. The promotion effect of the WOₓ is limited to the monolayer phase where synergistic interactions between it and Ni help maintain the WOₓ in a partially oxidized state with under-coordinated W cations that are the active sites for scission of the C-O bond in m-cresol.
Chapter 6 Conclusions

This dissertation has demonstrated the viability of utilizing bifunctional catalysts, which consist of a reducible metal oxide and a noble or base metal, to upgrade biomass-derived oxygenates, especially aromatic oxygenates from the lignin fraction. Gas-phase reactions were first used to investigate the catalytic performance of bifunctional catalysts, and surface sciences techniques such as TPD, HREELS, XPS provided insights into the underlying mechanisms and active sites of the reactions. These contributions should help in the development of commercial catalysts for biomass upgrading.

The work in chapter 3 provides experimental confirmation of the DFT predictions of Wang et al. [42] that interactions at the Pt-WO_x interface enhance the reducibility of submonolayer WO_x deposits and help maintain them in a partially reduced state, and that m-cresol adsorbs on undercoordinated W cations in the supported WO_x via the hydroxyl oxygen in a bonding configuration in which the aromatic ring is tilted away from the surface. The weak interaction between aromatic ring and Pt surface enhances the selectivity for C-O bond scission and also limits ring hydrogenation under typical HDO reaction conditions. In contrast, on the Pt(111) surface, a strong interaction between the Pt and the aromatic ring results in a bonding configuration where the ring lays flat on the surface. Under typical HDO reaction conditions where high H_2 pressures are used, this bonding configuration would be expected to facilitate ring hydrogenation.

Chapter 4 expands our previous mechanistic studies of the use of oxides to enhance the selectivity of Pt-based catalysts for the HDO of aromatic oxygenates to produce
aromatic hydrocarbons and to include the use of niobium oxide as the oxide modifier. NbOₓ−Pt/C was found to be highly selective for the HDO of m-cresol to produce toluene. The high selectivity to toluene (>95%) and the lack of a significant production of keto–enol and ring hydrogenation products indicate that the reaction proceeds via the direct hydrogenolysis of the C–O bond rather than by the tautomerization pathway that has been proposed for unmodified Pt catalysts. The model catalyst studies demonstrated that the interaction at the NbOₓ−Pt interface helps stabilize the NbOₓ in a partially reduced state, which contains undercoordinated Nb cations that provide bonding sites for the hydroxyl oxygen in m-cresol which is similar to that observed for the WOₓ modifier. Adsorption on these sites again produces a bonding configuration in which the aromatic ring is tilted away from the surface. This is in contrast to pure Pt surfaces in which there is a strong surface–ring interaction that results in a lay-flat adsorption geometry, which facilitates ring hydrogenation.

Considering the price of noble metals like, Pt and Pd, less expensive base metal, Ni, is taken into consideration. We expanded our studies of WOₓ- and NbOₓ-modified Pt catalysts described in Chapter 3 and 4 to the analogous WOₓ-modified Ni catalyst in order to explore whether high HDO selectivity can be obtained using this less expensive metal. It was observed that WOₓ-modified Ni/C catalysts are highly activity and selective for the HDO of m-cresol to produce toluene and methylcyclohexane. On the unpromoted Ni/C catalyst the HDO reaction proceeded via an indirect tautomerization pathway that produced significant amounts of methylcyclohexanone and methylcyclohexanol in addition to toluene and methylcyclohexane. This catalyst also promoted hydrogenolysis of C-C bonds at higher temperatures. Decorating the surface of the Ni with WOₓ significantly
enhanced HDO selectivity to toluene and methylcyclohexane and inhibited the activity for ring hydrogenation and C-C hydrogenolysis. At 623 K this catalyst achieved 89% selectivity to the desired toluene product. The lack of products with hydrogenated rings for this catalyst indicates that the reaction follows a direct HDO pathway. The promotion effect of the WO\textsubscript{x} is limited to the monolayer phase where synergistic interactions between it and Ni help maintain the WO\textsubscript{x} in a partially oxidized state with under-coordinated W cations that are the active sites for scission of the C-O bond in \textit{m}-cresol.

My mechanistic studies of highly active and selective metal-metal oxide catalysts to promote the direct deoxygenation of \textit{m}-cresol model compound to toluene provides the theoretical basis for future industrial production of toluene. What’s more, ideas behind my studies can be used to design other high performance HDO catalysts.
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