

**The Role of Oxophilic Metal Promoters in Bimetallic
Hydrodeoxygenation Catalysts**

by

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The Role of Oxophilic Metal Promoters in Bimetallic Hydrodeoxygenation Catalysts

Thesis directed by Prof. J. Will Medlin

In this thesis we investigate the role of oxophilic metal modifiers in deoxygenation catalysts, starting with surface science experiments and extending to supported catalyst studies.

Carbon-oxygen bond scission is critical for biomass upgrading applications, but these bonds tend to be strong in the aromatic oxygenates that make up a large portion of pyrolysis oil. Bimetallic catalysts containing a noble metal and an oxophilic metal have shown promising activity and selectivity for deoxygenation, but the role of each metal in the overall reaction is unclear. Gaining a fundamental understanding of the roles of oxophilic sites will facilitate a systematic approach to catalyst design.

Structure-property relations were investigated under ultra-high vacuum (UHV) using a Pt(111) single crystal modified with sub-monolayer quantities of molybdenum. X-ray photoelectron spectroscopy suggested that when the surface is pretreated in hydrogen the Pt and Mo sites interact, resulting in a significant electronic effect on the Pt atoms. Low energy electron diffraction indicated that the hydrogen-reduced surface is well ordered, with Mo atoms inserted into the Pt lattice. The electronic effect was apparent using temperature-programmed desorption (TPD) experiments; as the coverage of Mo increased the desorption temperatures of carbon monoxide and hydrogen decreased by 10 and 30 K, respectively. In addition, these reduced Pt-Mo sites were shown to allow dissociation of water into hydrogen and surface hydroxyls, a process that does not occur on unmodified Pt(111). This may be important for deoxygenation because surface hydroxyl groups may act as acid sites. Alternatively, when the surface was treated in oxygen, the oxidized Mo formed an inert, disordered surface layer that only served to block active sites.

To extend this approach to more complex reactants representative of pyrolysis oil, the surface chemistry of benzyl alcohol was studied using TPD. Pt(111) catalyzed both decarbonylation to

form benzene and carbon monoxide as well as complete decomposition to hydrogen and surface carbon. Incorporation of Mo improved the selectivity to hydrogenolysis, forming toluene as the major organic product. Toluene TPD and density functional theory (DFT) calculations suggested that the selectivity improvement may be in part due to reduced adsorption strength of the aromatic ring. These results were extended to alumina-supported Pt and PtMo catalysts. When Mo was incorporated into particles with a large fraction of terrace (111) sites the same shift in reaction pathway was observed as in the UHV results, with increased hydrogenolysis activity to produce toluene and lower activity for decarbonylation.

Supported Pt and PtMo catalysts were also studied for deoxygenation of m-cresol, an aromatic oxygenate containing a very strong C-O bond. Incorporation of Mo was found to increase selectivity to the deoxygenated alkane product. DFT calculations suggest this may be due in part to strong binding of the oxygen-containing functional group to the Mo site, resulting in an altered adsorption orientation that allows an additional deoxygenation pathway to be accessible by facilitating tautomerization.

Finally, preliminary studies have been performed to design an improved deoxygenation catalyst. The previous results suggest that two key influences of an oxophilic metal modifier are to reduce adsorption strength of carbon and to increase the strength of the interaction between the surface and the oxygen-containing moiety. DFT calculations were performed to calculate the difference in carbon versus oxygen adsorption strength on various bimetallic surfaces. Using this approach, several new bimetallic catalysts were identified as promising candidates, including PtW and PdFe. Preliminary evaluations of these catalysts suggest that by tuning this difference in adsorption strengths an improved deoxygenation catalyst may be synthesized.

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Chapter 1

Introduction

1.1 Motivation

Modern society relies heavily on catalysts for production of everything from transportation fuels and fine chemicals to consumer products and pharmaceuticals; the chemical industry uses catalysts for 85-90% of all products made [1]. The function of a catalyst is to increase the rate of a chemical reaction or set of reactions by lowering the activation energy [1]. It does so by providing a place for reactants to bind, allowing them to form lower energy transition states as they react to form products which can then leave the catalyst, which is not consumed and is used again to repeat the process in another reaction [1]. This may be done by a compound in the same phase as the reactants, known as a homogeneous catalyst, or by a compound in another phase, known as a heterogeneous catalyst. Many industrial processes utilize heterogeneous catalysts; a major advantage to these materials is that they can be easily separated from the products, which significantly lowers separation costs.

In addition to increasing the rate of chemical reactions, a major goal of catalyst design is to improve selectivity to desired products. Often many reactions may occur in parallel and targeting only one of them is difficult. Developing catalysts that can selectively produce a desired compound is important because separation processes to purify the product stream are both costly and energy intensive. While enzymes are known for being incredibly selective to a desired reaction pathway, many metal catalysts used industrially are much less so. Supported metals are more robust than biological catalysts, able to tolerate harsh reaction conditions and therefore be applied to many

processes, so there is great interest in making inorganic materials that can achieve high selectivity as well. Therefore, a primary focus of current catalysis research is in development of more selective heterogeneous catalysts.

One particular application for which selective catalysis is especially critical is in the production of biomass-derived fuels and chemicals. Increasing environmental and economic concerns surrounding fossil fuels have motivated a major research focus into development of renewable replacements. One of the most promising alternatives to petroleum for production of fuels, plastics, and chemicals is biomass. Upgrading of lignocellulosic biomass provides a unique opportunity to use waste materials and plants that do not compete with food production. Through fast pyrolysis, the biomass is rapidly heated in the absence of oxygen to produce a condensable mixture of oxygenates along with char and light gases [2–4]. Pyrolysis oil composition varies depending on the feedstock and process conditions, but contains high concentrations of phenolic compounds from lignin decomposition and furanic compounds derived from cellulose, in addition to organic acids and other low molecular weight oxygenates [5]. An example lignin structure along with some of the most prevalent compounds resulting from its pyrolysis are shown in Fig. 1.1.

The high oxygen content of lignin-derived compounds is undesirable for fuel application. Unfortunately, design of catalysts for oxygen removal is problematic due to the strong aromatic-oxygen bonds that are present. These complex, multifunctional oxygenates are also difficult to selectively upgrade into a desired final product because they may interact with a catalyst surface in multiple, often uncontrolled ways. Conversion of the compounds making up pyrolysis oil requires new types of catalysts that can selectively remove oxygen from the oil. A wide variety of materials has been studied for pyrolysis oil upgrading, ranging from carbides and nitrides to supported transition metals, but despite their diversity the most promising materials are bifunctional: they contain disparate active sites that catalyze complementary reaction steps. In many cases upgrading these multifunctional compounds demands a combination of different reactions to arrive at a desired product; it is natural that each step would require its own catalyst. Therefore, development of a bifunctional catalyst capable of selectively deoxygenating lignin-derived compounds represents a

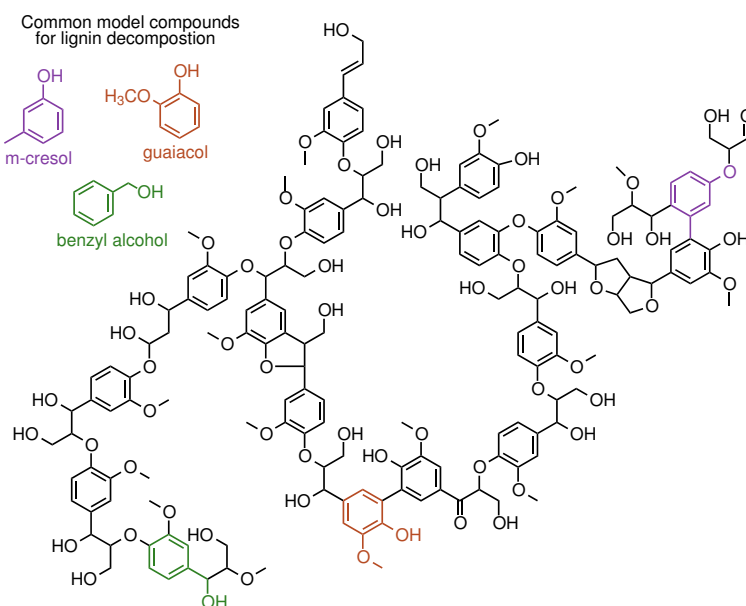


Figure 1.1: Partial structure of lignin, highlighting several model compounds that are often used to represent the lignin fraction of pyrolysis oil. From Ref. 6.

major focus of modern catalysis research.

1.2 Bifunctional catalysis overview and background

The general concept behind bifunctional heterogeneous catalysis is that there are two distinct types of active sites that function in tandem to perform a surface-catalyzed reaction. Often, these two types of sites are expected to catalyze different elementary steps within an overall reaction. In principle, however, the two sites could participate in the same step, for example through interaction of different parts of an adsorbed reactant molecule with the catalyst as in a concerted reaction. In this section, we highlight two major types of materials used as bifunctional catalysts before considering the application of similar types of materials in biomass refining reactions. Proposed mechanisms for two major classes of catalysts are shown schematically in Fig. 1.2a-b. To point out the connections between these examples for simple reactants of well-studied reactions and the oxygenate upgrading reactions of primary interest for this review, an example of bifunctional catalysts for deoxygenation of phenolic oxygenates is shown in Fig. 1.2c.

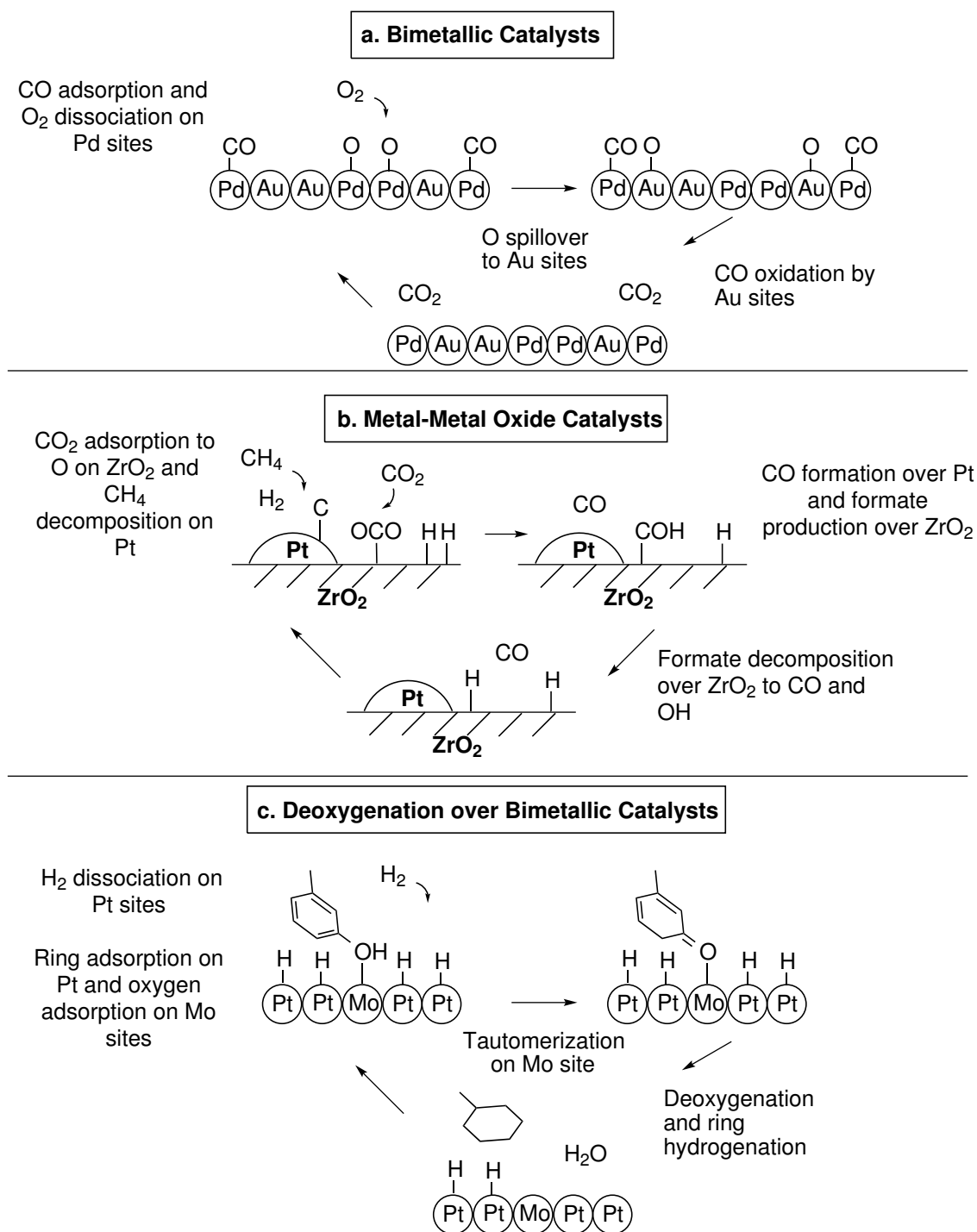


Figure 1.2: Schematic representation of proposed deoxygenation mechanisms by a) bimetallic catalysts [7], b) metal-metal oxide catalysts [8], and c) bimetallic catalysts specifically for deoxygenation [9].

The following sections will provide a brief literature review of these classes of bifunctional catalysts as an introduction to the investigations performed in this thesis. Specifically, they will provide an overview of the state-of-the-art for bifunctional supported catalysts.

1.2.1 Metal-metal oxide catalysts

A frequently used type of bifunctional catalyst combines metal sites that are active for hydrogenation/dehydrogenation and acid sites that are active for protonation/deprotonation. For example, catalytic metals may be supported on a zeolite. In the isomerization of alkanes, the saturated hydrocarbons are dehydrogenated to alkenes on the metal sites; the alkenes can subsequently migrate to acid sites, which protonate the alkenes to form carbenium ions [10]. Structural rearrangement of the carbenium ion can lead to formation of branched structures, which upon deprotonation yield branched alkenes. Finally, the branched alkenes are hydrogenated on metal sites. While these reactions can be catalyzed by physical mixtures of metal and zeolite catalysts, achieving intimate contact between the different types of reactive sites significantly improves the kinetics. Producing zeolite-supported metals with high dispersion is important for improving the intimacy of contact and achieving rapid isomerization kinetics [11].

The intimacy of metal-metal oxide contact has also been found to be important in other reactions, with considerable focus devoted to Au nanoparticles dispersed on reducible oxide supports [12]. For example, Au supported on ceria [13, 14] or titania [15] has been found to be active for the water-gas shift reaction at relatively low temperatures, ranging from approximately 473-623 K. The metal oxide support has been reported to be active for the required water dissociation step, whereas CO oxidation has been associated with sites at the Au-metal oxide interface. A related mechanism has been demonstrated on Pt/ZrO₂ catalysts for dry reforming of methane Fig. 1.2b. It was shown that the Pt metal serves to activate methane, dehydrogenating it to form CH_x, while sites at the Pt-ZrO₂ interface are responsible for CO₂ dissociation. Achieving good catalyst performance was found to require optimization of the interfacial contact area [8]. Furthermore, bifunctional metal - metal oxide catalysts in which the oxide serves as a base have also been reported. For example,

isobutanol may be produced using syngas (CO and H₂) on bifunctional catalysts consisting of Cu supported on basic metal oxides such as MgO [16]. The syngas initially forms alcohols that may be coupled through condensation reactions. In the proposed mechanism, the alcohol dissociatively adsorbs on the basic oxide surface, creating hydrogen and alkoxide species [16]. Hydrogen is removed by migration to Cu sites, where they recombine and desorb as H₂, while the alkoxide species may be further dehydrogenated and eventually take part in condensation reactions to form longer chain compounds [16]. Chain growth rates are low due to the steric hindrance that occurs as branches are added to the initially formed linear alcohols, resulting in production of isobutanol at high selectivity [16].

1.2.2 Bimetallic catalysts

One of the most common methods for controlling the catalytic performance of supported metal catalysts is via control over the composition of bimetallic catalysts. In a large number of cases, adding one metal to another is not intended to introduce a new catalytic function, but instead modifies the activity of the original metal. A second metal may influence the properties of the first via ligand effects, which is often interpreted in terms of a shifting of the d-band density of states of the first metal. A much-studied example of this phenomenon is in the performance of Pt "skin" catalysts that have been modified by 3d elements such as Ni, Co, Fe, and Ti in the subsurface for improved performance in the electrocatalytic oxygen reduction reaction [17–19]. In many of the systems dominated by this effect, the modifying metal is assumed to not be present in the surface layer, and thus has little opportunity to directly create a bifunctional effect [20]. Another mechanism by which addition of a second metal can modify a catalyst surface is via the so-called "ensemble" effect [21]. For example, addition of (relatively unreactive) Au to Pd olefin hydrogenation catalysts has yielded an improved activity that has been attributed to a decrease in the average number of contiguous Pd atoms; contiguous surface Pd clusters have been associated with accumulation of unreactive spectator species [22].

In some cases, however, the presence of two metals at the surface under reaction conditions has

been associated with a bifunctional effect. Bifunctional effects have been invoked, for example, in some studies involving PdAu catalysts. Xu and coworkers found that biphasic PdAu nanoparticles—where segregation of the two metals into relatively Pd-rich and Au-rich—were highly active for low-temperature CO oxidation [7]. The authors found that Pd-rich sites were needed to carry out the dissociative adsorption of oxygen, whereas Au-rich sites were active for CO oxidation, as shown schematically in Fig. 1.2a. The dispersion of the two metals in an active catalyst has been seen experimentally through STM images of PdAu alloy electrodes. In this example, PdAu thin films were electrodeposited on Au(111), resulting in Pd monomers, dimers, and trimers on the surface (Fig. 1.3) [23]. Scanning tunneling microscopy was used to obtain transmission microscopy images of different PdAu compositions, which were found to contain highly dispersed Pd atoms. This dispersion is correlated with activity in Fig. 1.3; the coverage of hydrogen and CO on the surface was measured along with the coverage of monomers, dimers, and trimers of Pd [23]. Because CO adsorbs on Pd sites, the coverage of CO increases with Pd loading. Furthermore, IR results showed that the CO adsorbed on a top site in these disperse samples, while large Pd clusters (or a pure Pd surface) had a high concentration of bridge/threefold bound CO [23]. This high dispersion creates many of the neighboring Pd-Au sites responsible for the bifunctional reaction shown schematically in Fig. 1.2a.

Similar effects have been proposed in olefin hydrogenation, where Pd sites are necessary for dissociative hydrogen adsorption while Au sites are active for hydrogenation [24]. Bimetallic catalysts have also been employed such that different types of sites are effective for reactions under different conditions. For example, PtAu nanoparticles have been applied as electrocatalysts for lithium-air batteries. The Au component was found to be more active for the oxygen reduction reaction (which occurs during battery discharging), while Pt sites were associated with the reverse oxygen evolution reaction (which occurs during charging) [25]. The utility of combining two active sites in one material has also been shown for use in unitized regenerative fuel cells (URFCs). These electrochemical cells operate in one mode to electrolyze water, producing hydrogen and oxygen, then operate in fuel cell mode to recombine them and produce electricity [26, 27]. The challenge with this

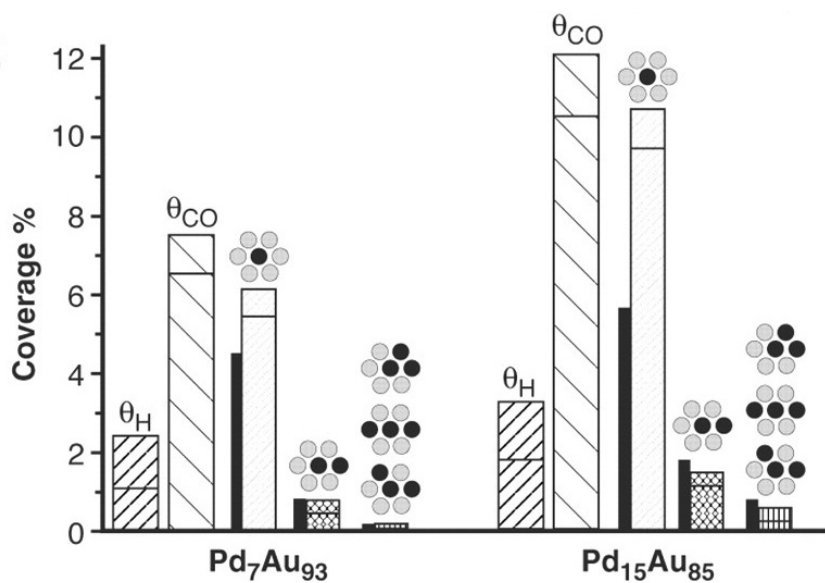


Figure 1.3: The surface coverage of monomers, dimers, and trimers of Pd for two surfaces along with experimental results for the coverage of H and CO on these two electrodes. Reprinted from [7].

concept is designing an electrocatalyst that is active for all of the reactions involved; catalysts active for the oxygen reduction reaction (ORR) perform poorly for the oxygen evolution reaction (OER) [26, 27]. Finding a catalyst that is both stable and active for OER, which involves oxidizing water to molecular oxygen in acidic media, has represented a major research focus in electrocatalysis. This is due in part to the limited studies on the relationship between catalyst active site structure and OER activity [28]. While Pt is nearly ideal for ORR, it has shown poor OER activity. Deactivation occurs due to reduced surface area and formation of a poorly conductive PtOx layer, which requires liberated electrons to tunnel through and therefore exponentially reduces current as a function of thickness [29]. This may be overcome by using a bifunctional catalyst consisting of the conventional Pt particles used for ORR supported on an oxide such as IrO₂ for the oxygen evolution reaction [26, 27].

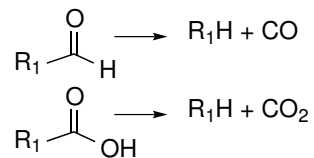
1.2.3 Importance of bifunctionality for biomass reforming

A common theme across the classes of materials studied for biomass deoxygenation is their bifunctionality. As discussed in the next section, the importance of having sites capable of activating hydrogen in close proximity to sites that are effective for C-O scission has been proposed many times throughout the literature for materials ranging from supported transition metals to traditional hydrotreating catalysts such as sulfides [30–42]. Often these two reaction steps cannot be effectively catalyzed by one type of active site. As a result, the most commonly proposed mechanisms for deoxygenation of these compounds involve one active site (such as a transition metal) that readily activates hydrogen and another type of site nearby, such as an acid site on an oxide support, for C-O bond activation. While this can be studied using whole pyrolysis oil, the complex mixture of oxygenates present makes it very difficult to elucidate reaction pathways to understand mechanisms. For this reason it can be useful to instead consider more detailed studies using model compounds. Phenolic compounds are useful probe molecules for pyrolysis upgrading reactions; they make up a large fraction of the oil and the C-O bonds in these molecules are very difficult to break [31, 43–45]. Other processes more representative of alternative conversion approaches, such as aqueous phase processing of polyols, are also described below.

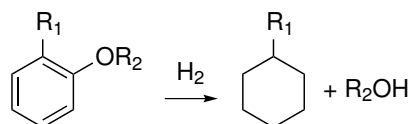
One common strategy for deoxygenating whole pyrolysis oil is hydrodeoxygenation (HDO), which involves adding hydrogen to accomplish C-O bond scission via removal of water. This is typically done sequentially, with a hydrogenation-dehydration-hydrogenation route in which dehydration often occurs over an acid site. Alternatively, direct deoxygenation (DDO) does not require intermediate hydrogenation steps; instead, the C-O bond is directly cleaved from the reactant through hydrogenolysis. It should be noted that while HDO reactions often produce saturated compounds and DDO may lead directly to aromatic compounds, aromatic and saturated products can also be interconverted subsequent to being formed. For example, increasing the temperature shifts the thermodynamic equilibrium towards aromatic products such as toluene production over methylcyclohexane. Other reactions can also take place under these conditions,

including decarboxylation/decarbonylation, cracking, and hydrogenation [46, 47]. Examples of these reactions are shown in Fig. 1.4.

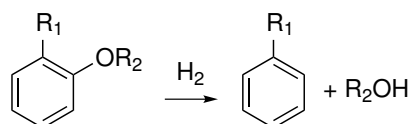
Decarbonylation/Decarboxylation



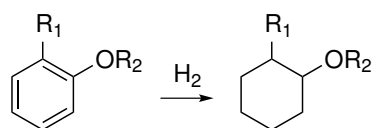
Hydrodeoxygenation



Direct Deoxygenation



Hydrogenation



Cracking

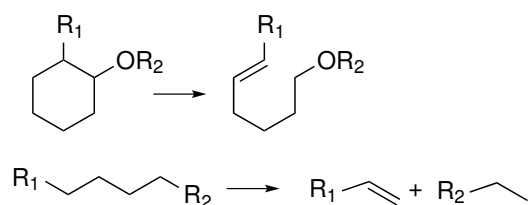


Figure 1.4: Example reactions discussed in this review.

1.3 Literature review of bifunctional catalysts for deoxygenation

1.3.1 Monometallic catalysts

Before discussing the use of bimetallic catalysts for deoxygenation applications it is useful to understand what has been done with single metals on various supports. The combination of a transition metal and a support, particularly an oxide with acid sites, has been studied extensively in the literature. While it is difficult to directly compare the variety of different catalysts tested under varying reaction conditions, it may be informative to look at general trends in performance that has been observed in the literature. Fig. 1.5 shows the selectivity to deoxygenated products when feeding aromatic oxygenates including cresol and guaiacol.

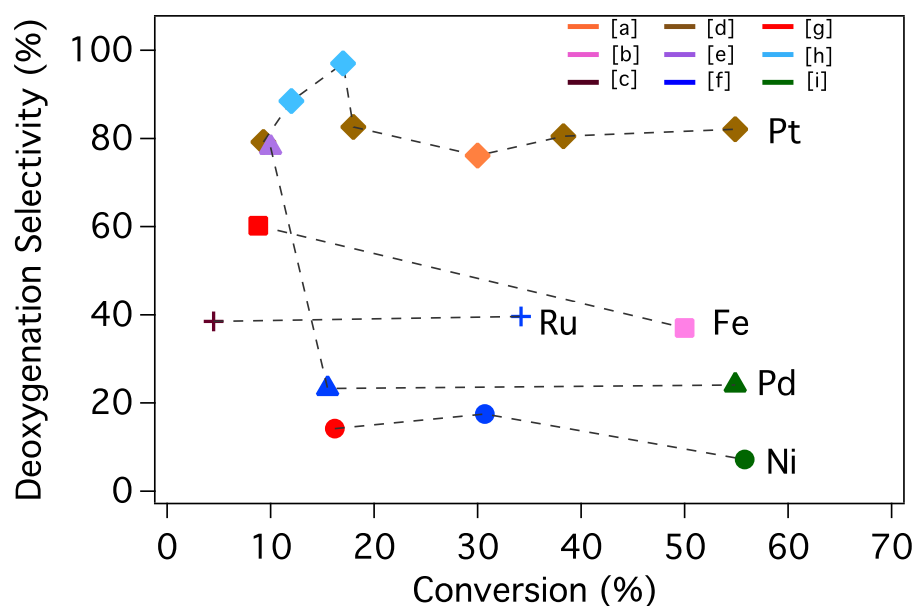


Figure 1.5: Selectivity to deoxygenated products from feeding vapor phase aromatic oxygenates (cresol or guaiacol) over Pt (diamonds), Ru (crosses), Fe (squares), Pd (triangles), and Ni (circles) catalysts. Color indicates the reference the data point was taken from: a. [30], b. [48], c. [49], d. [31], e. [50], f. [51], g. [32], h. [52], i. [53]

Across a range of conversions, Pt catalysts appear to have the highest deoxygenation selectivity of these monometallic samples. The data used in this figure can also be seen in Table 1.1. However, the performance of these monometallic catalysts can be dramatically changed through

incorporation of a second metal, as will be discussed below.

Table 1.1: Data used in Fig. 1.5 to compare selectivity to deoxygenation of m-cresol or guaiacol over various supported metals.

Catalyst	Temperature (K)	Pressure (MPa)	Partial Pressure of H ₂ (MPa)	wt% metal	Reactant	Conversion (%)	% deoxy-genation	Reference
Pt/Al ₂ O ₃	533	0.1	0.05	0.5	m-cresol	9.3	79.2	[31]
Pt/Al ₂ O ₃	533	0.1	0.05	1	m-cresol	18	82.6	[31]
Pt/Al ₂ O ₃	533	0.1	0.05	1.7	m-cresol	38.3	80.5	[31]
Pt/SiO ₂	533	0.1	0.05	1.6	m-cresol	54.9	82.1	[31]
Pt/Al ₂ O ₃	533	0.1	0.05	1.7	m-cresol	30	76.1	[30]
Pt/TiO ₂	573	0.1	0.1	1	m-cresol	17	97	[52]
Pt/ZrO ₂	573	0.1	0.1	1	m-cresol	12	88.5	[52]
Ni/SiO ₂	523	0.1	0.1	5	m-cresol	55.8	7.2	[53]
Ni/C	623	4	3.8	5	guaiacol	30.7	17.5	[51]
Ni/SiO ₂	573	0.1	0.1	5	m-cresol	16.2	14.2	[32]
Pd/C	573	0.1	0.04	5	m-cresol	10	78	[50]
Pd/SiO ₂	523	0.1	0.1	1	m-cresol	54.9	24.1	[53]
Pd/C	623	4	3.8	1	guaiacol	15.5	23.3	[51]
Fe/SiO ₂	573	0.1	0.1	5	m-cresol	8.8	60.2	[32]
Fe/SiO ₂	623	0.1	0.09	-	guaiacol	50	37	[48]
Ru/SiO ₂	573	0.1	0.1	9.4	m-cresol	4.5	38.5	[49]
Ru/C	623	4	3.8	1	guaiacol	34.2	39.6	[51]

To better understand reactivity trends for these systems, it is often useful to study reactivity on model surfaces such as single crystals. Reactions of simple organic oxygenates that can serve as probe molecules for components in deconstructed biomass have been extensively studied using surface spectroscopies and model surfaces. There have been past reviews focusing on the decomposition of simple oxygenates including alcohols, aldehydes, ketones, and carboxylic acids over transition metal surfaces [54–57]. For example, formic acid decomposition has been studied as a probe for organic acids. A past review of surface science studies over single crystals focused formic acid adsorption and decomposition processes [54]. Formic acid tends to decompose through a formate intermediate. The formation of a carboxylate intermediate has been observed for larger carboxylic acids as well, over a wide array of transition metals [57]. Formate decomposition can then occur either through dehydrogenation to produce CO₂ and H₂, or C-O scission to form CO and H₂O [54]. The pathway that a given transition metal will favor depends on how strongly it

binds oxygen: metals like Pt that form relatively weak metal-oxygen bonds favor dehydrogenation [58] while metals further left on the periodic table such as Fe favor C-O scission [59]. On Pd(111) both pathways were observed, although selectivity was greater towards dehydrogenation [60]. On Ni(111) the binding configuration was proposed to be different, creating formic anhydride as an intermediate, but the dominant decomposition pathway was C-O scission [61]. A major conclusion from these studies is that C-O bond scission is often not favored on metals like Pt and Pd that do not strongly bind oxygen, even when the C-O bond is relatively weak. Similar observations have been made for reactions of other oxygenates such as alcohols and aldehydes. On noble metals such as Pt and Pd, decarbonylation via C-C scission is often a dominant pathway, and C-O scission is generally not observed [55]. An exception is the reaction of unsaturated alcohols and aldehydes such as prenal, furfural, and benzyl alcohol, where the C-O bond is much weaker than in aliphatic or phenolic reactants. However, noble metals are attractive for their ability to activate hydrogen and to conduct hydrogenation reactions. This suggests that deoxygenation for reforming pyrolysis oil may be best accomplished using a bifunctional catalyst that combines these hydrogenation sites with sites that form strong metal-oxygen bonds to facilitate C-O bond cleavage. The impact of metal-oxygen bond strength will be discussed further below.

This hypothesis is also supported by studies of technical catalysts composed of combinations of metal and acid sites. Late transition metal catalysts have several properties that make them potentially attractive for pyrolysis oil upgrading; they are typically very active, are effective at hydrogenation, and have well characterized structures. Additionally, they do not suffer from some of the issues of traditional hydrotreating catalysts, such as the need for co-feeding toxic H_2S to maintain activity as for sulfides [62]. When an active support material is used to impart bifunctionality these catalysts can be used for HDO of relatively recalcitrant compounds such as phenolics. Before discussing the bifunctional materials, it is useful to first discuss the individual components as supported monometallic catalysts.

Noble metals including Ru, Rh, Pd, and Pt are a class of promising upgrading catalysts; they activate hydrogen, are not deactivated by water, and are already widely used in commercial catalytic

processes [63]. Under typical upgrading conditions the differences in the chemistry catalyzed by the various noble metals are subtle, with similar reaction pathways and products [47], and these materials have been highlighted in a number of reviews discussing pyrolysis oil upgrading [2, 37, 46, 47, 64]. As an illustration of their HDO activity as monofunctional catalysts, Pd/C, Pt/C, and Ru/C were studied for vapor phase guaiacol (2-methoxyphenol) HDO [65]. While the hydrogenation activity was high, the paper concluded that carbon-supported noble metals are poor HDO catalysts because they favor ring saturation over deoxygenation. At 523 K the C-O bond between the ring and methoxy group was broken, but C-O scission of the strong aromatic-hydroxyl bond did not readily occur, producing phenol as the major product [65]. Additionally, ring hydrogenation to form cyclohexanone and cyclohexanol occurred, and a small amount of benzene was formed as well [65]. Even by varying reaction conditions, for instance by using elevated temperature and pressure (623 K and 4 MPa), noble metal catalysts show poor selectivity to complete deoxygenation [51].

Supports with acid/base activity have been widely used to achieve better deoxygenation yields from phenolic reactants. The aromatic-O bonds of phenolic compounds are weakened following ring hydrogenation, aromatic-OH bonds have a bond dissociation energy of about 486 kJ/mol while alkane-OH bonds have a dissociation energy of about 385 kJ/mol [38]. This weakening of the C-O bond has led to the hypothesis that the deoxygenation mechanism over noble metals involves hydrogenation followed by dehydration rather than direct C-O scission [30–32]. In this model, one site is proposed to activate C-O bonds. This component is often proposed to be a Brønsted acid site on the oxide support materials. In addition, sites are needed to supply atomic hydrogen to the reaction; this role is played by the noble metal [37]. The proposed mechanism of hydrogenation followed by dehydration is shown in Fig. 1.6. The deoxygenated product is shown converting between the aliphatic and aromatic compound to highlight that depending on the reaction conditions either may be formed. Aromatic oxygenates may be fully saturated over the metal particles, particularly if the reaction conditions favor this (i.e., at lower temperatures, where thermodynamic equilibrium favors saturated products) [30, 31].

M = transition metal or bimetallic particle

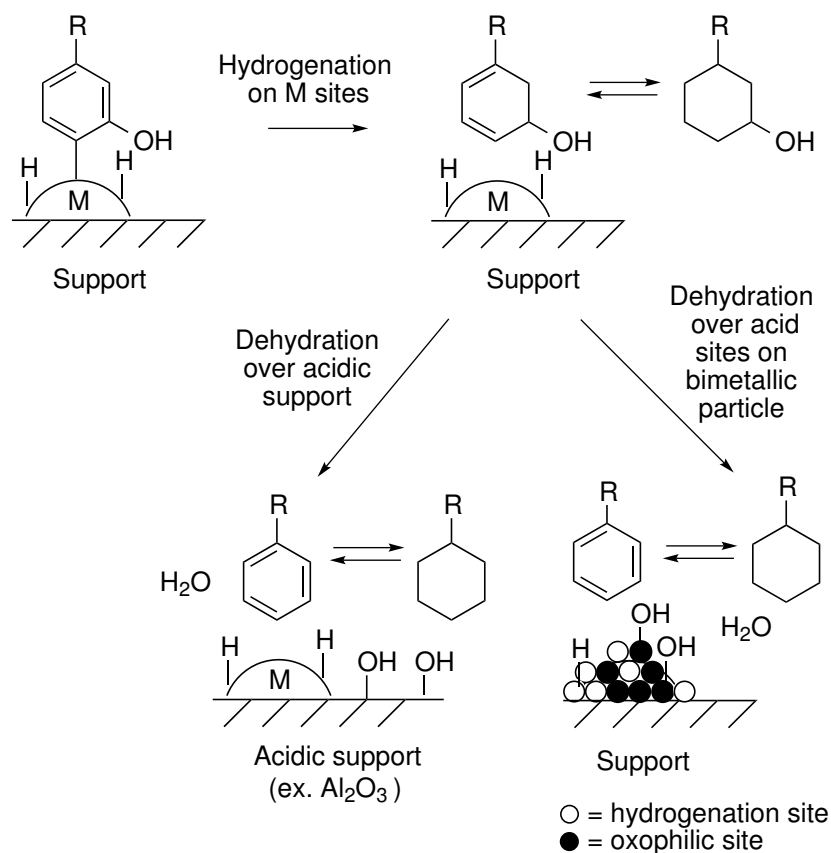


Figure 1.6: Schematic representation of metal-acid catalysis proposed for aromatic deoxygenation on noble metal based catalysts.

One report studying the vapor phase HDO of m-cresol (3-methylphenol) over $\text{Pt}/\text{Al}_2\text{O}_3$ found that a bifunctional mechanism was required, involving hydrogenation activity to form alcohol intermediates as well as acidity for dehydration [30]. It was proposed that ring hydrogenation first occurs to saturate the phenyl ring and a partially or fully hydrogenated alcohol intermediate is formed. On $\text{Pt}/\text{Al}_2\text{O}_3$ the partially hydrogenated alcohols may then deoxygenate on acidic sites on the support to form toluene [30]. This hypothesis was further supported by reacting the fully hydrogenated alcohol intermediate (3-methylcyclohexanol) on a bare Al_2O_3 support, where it was deoxygenated to form methylcyclohexene isomers [30]. The rate was much higher when the saturated intermediate 3-methylcyclohexanol was fed compared to the rate when m-cresol or

an alkene was fed. This result suggested that at 533 K ring hydrogenation over Pt sites to form the alcohol intermediates was rate limiting. The proposed rate-limiting step of ring hydrogenation was used to explain the higher selectivity of Pt/Al₂O₃ towards toluene than methylcyclohexane, because fewer steps are required to dehydrate the unsaturated alcohol intermediates than to produce saturated alkanes. Note that this mechanism requires intimate contact between the hydrogenation and deoxygenation sites. Also, despite bare γ -alumina easily catalyzing dehydration of the saturated alcohol no reaction was observed when feeding m-cresol; at least partial hydrogenation was required to allow cleavage of the C-O bond [31]. To improve the HDO activity, Ni and Co were added; these 3d metals have previously been shown to increase hydrogenation activity of unsaturated compounds [66]. By further increasing the hydrogenation activity of Pt through these bimetallic catalysts the HDO activity increased and the product distribution shifted to produce more methylcyclohexane relative to the amount of toluene formed. Total deoxygenation also increased over the bimetallic catalysts, proposed to be a result of generating aluminate species through interaction between the 3d metal and the support, which are active for alcohol dehydration [30].

Pt/SiO₂ was also studied to compare the alumina-supported material to a less acidic catalyst [31]. While both contain acid sites, the Lewis and Brønsted acidity on Al₂O₃ [67, 68] is stronger than that of SiO₂ [69]. The less acidic Pt/SiO₂ was found to be ineffective at dehydrating 3-methylcyclohexanol to the alkane product. A kinetic study of Pt/SiO₂ also concluded that this dehydration pathway is limited [52]. The dominant deoxygenation pathway was instead proposed to be dehydration of unsaturated alcohol intermediates to form toluene. While SiO₂ alone was not active for dehydration of 3-methylcyclohexanol, in the presence of Pt its weakly acidic hydroxyl groups can dehydrate partially hydrogenated alcohol intermediates present on the Pt particles as shown in Fig. 1.6 [31]. Both the Pt and SiO₂ sites are necessary for this reaction. When the support was doped with potassium to suppress the acidity the product distribution was substantially altered. Rather than primarily toluene, m-cresol formed 3-methylcyclohexanol with 84% selectivity [31]. This is in agreement with DFT calculations over Pt(111), which show that m-cresol HDO is less energetically favorable than ring hydrogenation [49]. However, increasing the reaction

temperature may increase the favorability of the HDO pathway over the hydrogenation pathway by both shifting the thermodynamic equilibrium between hydrogenation/dehydrogenation and by reducing the surface coverage of H [53].

Another study of support effects on noble metals also concluded that acidic supports facilitate phenolic HDO. Pt, Rh, Pd, and Ru supported on Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, and nitric-acid-treated carbon black (NAC) were studied for the liquid phase batch upgrading of guaiacol [33]. The support was found to have a greater influence on the product distribution than the noble metal. Using ammonia TPD, the acidity of the catalysts was found to decrease in the order $\text{SiO}_2\text{-Al}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{NAC}$ [33]. The same trend was found in production of cyclohexane, the fully deoxygenated and hydrogenated product, with selectivity decreasing in the order $\text{SiO}_2\text{-Al}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{NAC}$. The least acidic catalysts, those supported on NAC, had the highest yields of 2-methoxycyclohexanol, a result of ring hydrogenation without any C-O scission and an indication of low HDO activity [33]. Therefore, HDO was again proposed to need a bifunctional catalyst where acid sites are required to produce a deoxygenated product rather than stop at a ring saturated oxygenate.

In addition to HDO through hydrogenation reactions followed by dehydration, direct deoxygenation (DDO) has been observed over supported metal catalysts. As shown in Fig. 1.4, DDO does not require intermediate hydrogenation steps; instead, the C-O bond is directly cleaved from the aromatic reactant. This may be desirable for reducing the hydrogen demand of the deoxygenation process. One example of DDO is using noble metals supported on reducible oxides such as TiO_2 . For instance, Ru/ TiO_2 has been shown to catalyze DDO of phenol to benzene through a bifunctional mechanism at the interface between the metal and oxide [70, 71]. Using both experimental and computational techniques it was demonstrated that at 573 K and 3.8 MPa, water that is present on the TiO_2 may either accept or donate protons across the metal-metal oxide interface. This allows the phenolic OH group to be directly removed through donation of a proton, shown in Fig. 1.7. Although this is typically difficult to achieve due to the strong aromatic-oxygen bond, the bifunctional sites present at the interface containing both metal and acid functionalities were calculated to have a lower energy barrier than hydrogenation. On large Ru particles, where

the interfacial area is much smaller, ring hydrogenation was found to be most favorable as expected from previous studies of noble metals. Isotopic labeling experiments in combination with DFT calculations indicated that the Ru particles bind the phenol and activate hydrogen to catalyze the hydride attack (which regenerates the water co-catalyst on the support) while Brønsted acidic water on TiO_2 catalyzes C-O scission.

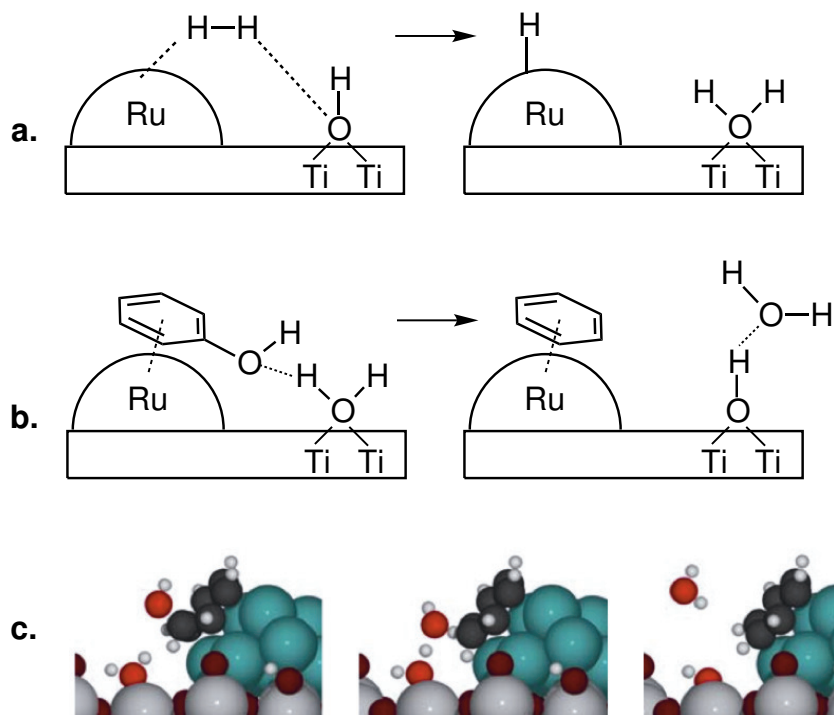


Figure 1.7: Proposed mechanism of DDO at the bifunctional Ru/TiO₂ interface. (a.) H₂ is activated on Ru particles and heterolytically dissociates across the interface to protonate a bridging hydroxyl group on TiO₂, generating a Brønsted acid site. (b.) This then assists in phenol deoxygenation. (c.) Side view of DFT calculation of water-assisted phenol DDO on Ru/TiO₂, including initial state (left panel), transition state (center panel), and final state (right panel). Color code: hydrogen, white; oxygen, red; carbon, dark gray; ruthenium, teal; titanium, light gray. Reproduced from [70]

This illustrates the importance of better understanding the metal-support interface, especially for reducible metal oxides like TiO₂ that may act as either an acid or a base. Similar results have been observed for Pt/TiO₂. The combination of a metal and a reducible oxide support were shown to enhance m-cresol deoxygenation by introducing additional energetically favorable reaction

pathways [72]. While Pt/C preferred ring hydrogenation, Pt/ TiO₂ catalyzed tautomerization and DDO. This synergistic effect was particularly important at elevated temperatures (623 K) [72].

While supported noble metal catalysts are promising for biomass HDO, their high cost has sparked interest in studying less expensive base metals such as Ni, Co, and Fe. Fe/SiO₂ was used for the gas-phase upgrading of guaiacol as a model compound to study iron's ability to break hydroxyl and methoxyl bonds on an aromatic ring [73]. The catalyst was found to be selective for production of aromatic hydrocarbons over a range of temperatures [73]. Kinetic studies of Fe/SiO₂ for guaiacol upgrading have also been performed [48]. Results from Fe catalysts were compared to the same reaction over a Co catalyst. Cobalt was found to be more active than Fe, but was shown to catalyze decomposition of the desirable products [48]. A simplified pathway is shown in Fig. 1.8. Transalkylation reactions were proposed to occur over the acid sites, explaining the formation of toluene from guaiacol.

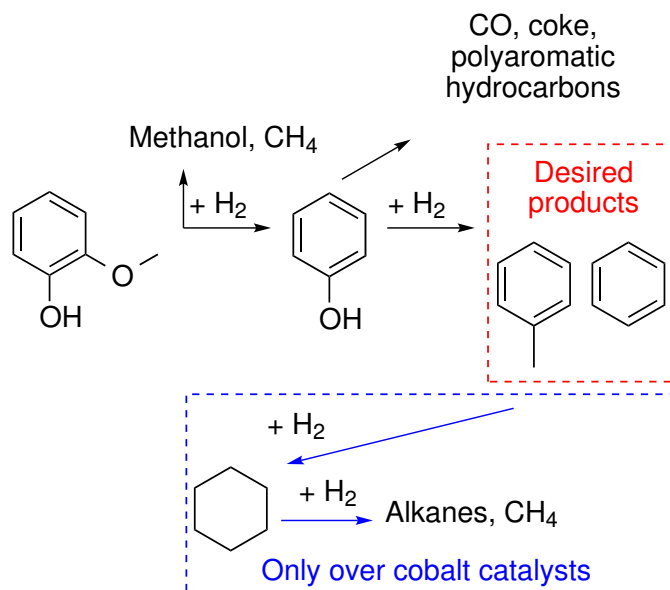


Figure 1.8: Simplified pathway of guaiacol HDO on iron and cobalt catalysts. Both iron and cobalt catalysts follow black arrows, only cobalt catalyzes additional reactions shown in blue. Adapted from [48]

A study comparing carbon-supported Fe and Cu to noble metals obtained similar results for

guaiacol HDO [65]. Guaiacol HDO was found to proceed through a phenol intermediate over all catalysts, but unlike the noble metals these base metals did not lead to ring hydrogenation and C-C scission products. For example, Fe/C was able to convert some of the phenol to aromatic deoxygenated products such as benzene and toluene [65]. However, the activity of the base metal catalysts was lower than the noble metals. On Pd, Pt, and Ru the intermediate phenol was primarily hydrogenated to form cyclohexanone and cyclohexanol as expected in the absence of an acid site for deoxygenation. In addition, ring opening to form light gases also occurred. Meanwhile, Fe and Cu were not active for ring saturation and ring opening reactions, predominately forming benzene [65]. This proposed network can be seen in Fig. 1.9.

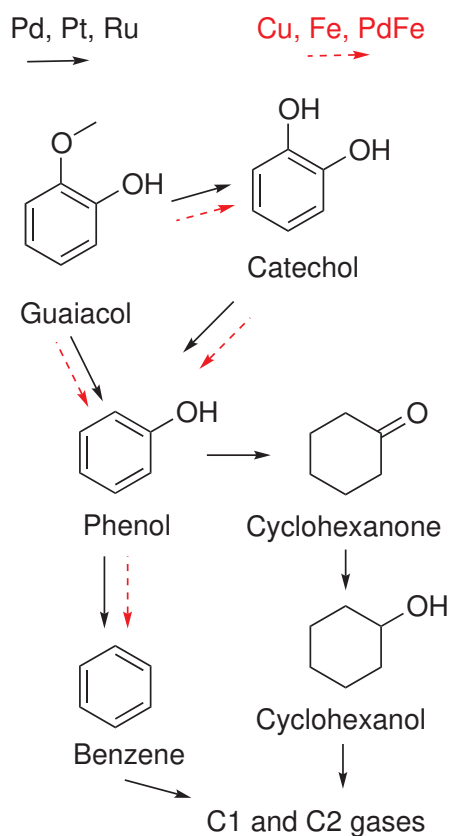


Figure 1.9: Proposed reaction network for guaiacol HDO on precious metals (Pd, Pt, Ru, pathways shown with solid black arrows) and base metals (Cu, Fe, pathways shown with dashed red arrows). Adapted from [65]

Although the previous literature convincingly demonstrates that a combination of acid

and metal sites leads to more complete deoxygenation, it is important to point out that metals themselves have some activity toward HDO reactions. For reactants with relatively weak C-O bonds such as allyl alcohol, furfuryl alcohol, and benzyl alcohol, HDO can even be observed on single crystals in ultrahigh vacuum [74–76]. Deoxygenation of these compounds on supported metals has often not been interpreted in terms of the support having a role. Studies of such reactants on supported Pd catalysts have shown that selective poisoning of different types of Pd sites can be used to favor selectivity for deoxygenation [77, 78].

1.3.2 Bimetallic catalysts

The previous examples of transition metal catalyzed HDO of phenolic compounds show that these catalysts may be promising materials for pyrolysis oil upgrading if acid sites are present. This mechanism (as shown in Fig. 1.6) may also take place over bimetallic catalysts. Oxide supports such as alumina are often used as the source of acid sites but they also can strongly bind oxygenates like phenols, leading to intermediates that block sites and can be precursors to coke formation [31, 79, 80]. Phenols and polyphenols have been shown to be coke precursors over a wide range of catalysts, including supported metals, oxides, and zeolites [81]. This has prompted studies of the effects of bimetallic catalysts containing a hydrogenating metal and an oxophilic metal (an element that forms especially strong metal-oxygen bonds compared to other metals) to provide intimate contact between diverse sites for pyrolysis oil upgrading [82]. Many of these have been noble metal-based alloys. Fig. 1.10 shows one proposed mechanism for the interaction of these bimetallic catalysts with an organic oxygenate. The metals used as a modifier site may be present in their metallic state or as an oxide; regardless, their role is to introduce an additional active site to produce a bifunctional metal particle. Table 1.2 shows metal-oxygen bond strengths for some commonly used oxophilic modifiers.

The hydrogenating sites provide H while the oxophilic metal more strongly binds the reactant to the surface through its oxygen functionality, allowing easier C-O scission and potentially creating new reaction pathways unavailable on a monometallic catalyst. The majority of bimetallic catalysts

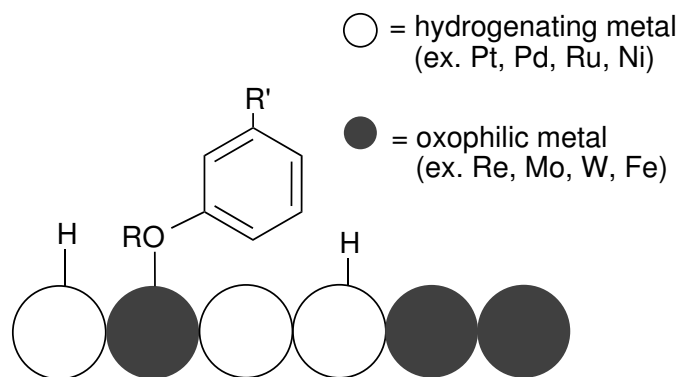


Figure 1.10: Hypothesized mechanism for interaction of oxygenates with bimetallic surfaces containing a metal capable of dissociating hydrogen and a metal that forms strong M-O bonds.

Table 1.2: Metal-oxygen bond strengths for oxophilic metals used in bimetallic catalysts. Values represent the bond dissociation energies measured at 298 K. Both modifier sites used as the oxophilic site and hydrogenating metals are included for comparison.

Metal-Oxygen Bond	Bond Strength (kJ/mol)	Reference
Oxophilic metals		
Co-O	397.4	[83]
Cr-O	461	[83]
Fe-O	407	[83]
W-O	653	[84]
Mo-O	607	[84]
Re-O	644	[85]
Hydrogenating metals		
Ni-O	366	[83]
Pd-O	234	[84]
Pt-O	347	[84]
Rh-O	377	[84]

investigated have involved 3d metals as a modifier to noble metals. These systems are known to create subsurface alloys with the surface noble metal atoms electronically modified [86, 87]. Subsurface transition metal alloys have been shown to increase HDO activity as well as selectivity towards saturated hydrocarbons [30, 66, 88, 89]. DFT results predict that the Pt terminated alloys bind adsorbates less strongly than pure Pt, resulting in a more optimized adsorption strength which increases hydrogenation [30]. An investigation of the hydrogenation of the unsaturated compounds benzene and 1,3-butadiene over Pt and PtNi catalysts also observed that hydrogenation

rates increased with the Ni loading [89]. DFT calculations have suggested this could be due to shifting the d-band center of surface Pt atoms by subsurface Ni, resulting in weaker binding of the unsaturated compounds [90]. The hydrogenation activity was shown to have a volcano curve-type relationship with the binding energy of the reactant [90]. Therefore tuning of this binding strength allows maximization of the hydrogenation activity. In addition to influencing hydrogenation rates, it was proposed that the bimetallic catalysts contained additional sites for dehydration. Metals such as Co and Ni can create additional acid sites through interaction with the alumina support to increase the rates of dehydration reactions [30]. This is proposed to be due to formation of an aluminate species, which previous work has shown increases the acidity on alumina [91]. Because acid-catalyzed dehydration steps are critical for C-O scission in phenolic compounds, this increases HDO rates.

Many previous studies with bimetallic catalysts have been performed using probe molecules such as glycerol. While the precise role of the modifier is unknown, many studies have shown increased activity and selectivity for C-O bond scission reactions for a variety of probe molecules and metal combinations [35, 92–96]. PtRe/C catalysts were shown to be more active than monometallic Pt for converting glycerol to syngas [35]. Here, the role of the oxophilic metal may not be directly related to its affinity for oxygen. Rather, CO-TPD showed that CO binding energies were reduced on PtRe compared to either monometallic sample, suggesting that reduced site blocking could be at least partially responsible for the increased activity [35]. Another glycerol reforming study in which PtRe/C was used for hydrogenolysis to form propanediols reported both increased rate and selectivity towards deoxygenation of the secondary alcohol [35]. Similar results were obtained for RhRe/SiO₂ catalysts [92]. In trying to understand the nature of these modifier sites, two main hypotheses have been proposed. First, it was suggested that hydroxylated Re-OH groups may be responsible for C-O activation by acting as Brønsted acid sites, with the strong metal-oxygen bond weakening the hydroxyl’s oxygen-hydrogen bond, thus allowing the hydrogen to be more easily donated to a neighboring oxygenate [35]. NH₃ TPD has shown increased acidity on PtRe catalysts in the presence of water relative to what is observed over the monometallic Pt sample

[97]. The second hypothesis is that these oxophilic sites are strongly anchoring the reactant to the catalyst surface through its oxygen functionality, allowing surrounding sites to donate hydrogen for deoxygenation [92]. This strong interaction of the oxophilic site and the oxygenated reactant can result in altered reaction pathways. For example, m-cresol was shown to preferentially follow the ring hydrogenation route to deoxygenation over pure group VIII metals such as Ni, Pd, and Pt (shown by the saturated compounds in Fig. 1.6) [32, 72]. However, when an oxophilic modifier was added to the catalyst a tautomerization pathway became available, creating a keto intermediate which may then be dehydrated to form toluene. By making this additional deoxygenation pathway energetically favorable the deoxygenation activity is increased. This has been shown for m-cresol HDO over PtMo/Al₂O₃, as illustrated in Fig. 1.2c [9].

Although more work is needed to fully understand the role of oxophilic modifiers, model compound studies show their promise for biomass deoxygenation. In addition to improving deoxygenation selectivity, some studies using bimetallic catalysts also reported DDO mechanisms. This is advantageous if the goal is to remove oxygen with minimal hydrogen consumption. Increased selectivity to C-O scission products has been observed over noble metal catalysts modified with oxophilic metals such as Fe, Re, Mo, and W; the modifier sites could potentially bind oxygenates more strongly to the surface or create acid sites when they are hydroxylated by water present under typical reaction conditions [35, 64, 93, 94, 96, 98, 99].

In one study, PdFe alloys were used for the vapor-phase upgrading of guaiacol [65]. PdFe/C showed better selectivity towards production of deoxygenated aromatics than either of the monometallic catalysts, and no ring saturation or ring opening products were observed. This study led to the hypothesis that phenolics prefer to adsorb on the Pd-modified Fe sites. Compared to the monometallic Fe surface, these sites hypothetically have altered electronic properties and are in a more reduced state due to increased hydrogen activation by Pd. This results in a catalyst that can activate phenolic C-O bonds without first needing to saturate the ring. This mechanism was explored through DFT calculations by substituting Pd atoms into a Fe(110) surface. Phenol was adsorbed with varying distances from the Pd atoms. The results indicated that adsorption and

C-O cleavage are both more favorable on the Fe sites [65]. TPR results on the PdFe/C catalysts showed that Pd assists in the reduction of FeO_x [65]. This evidence, along with EXAFS and STEM/EDS results, was used to propose that Fe is the active site for HDO and the role of Pd is facilitating reduction of FeO_x as well as modifying the Fe sites through electronic effects due to alloy formation [65]. Similar results were obtained from a Pd/ Fe_2O_3 catalyst for HDO of m-cresol: Pd was proposed to activate hydrogen and allow reduction of the Fe_2O_3 as well as prevent oxidation by water formed during the HDO reaction [97]. Addition of Pd was also found to increase the activity compared to monometallic Fe while maintaining a similar selectivity towards the production of aromatic deoxygenated products [97].

Cyclic oxygenates have also been studied for selective hydrogenolysis on bimetallic catalysts. A common conclusion among many of these reports is that the combination of a noble metal and an oxophilic metal such as Re, Mo, or W can dramatically increase selectivity to cleaving more sterically hindered C-O bonds. For example, Rh catalysts were modified with Re to improve selectivity to 1,6-hexanediol production from tetrahydropyran-2-methanol (THPM) [100, 101]. While Rh/C had only 15% selectivity to this desired product, Rh- ReO_x /C had 96% selectivity as well as increasing the reaction rate from 2 to 180 mmol-h⁻¹-g catalyst⁻¹. This improved activity was proposed to be due to increased coverage of adsorbed THPM on the ReO_x modified catalyst because the Re sites may strongly bind OH groups and allow an alkoxide species to form, strongly tethering the THPM to the surface. By adsorbing to the ReO_x through its OH group and forming this alkoxide, hydrogenolysis of the C-O bond adjacent to the alkoxide group is favored and therefore results in high selectivity to 1,6-hexanediol [100]. A similar mechanism was proposed using Rh- ReO_x /SiO₂ for tetrahydrofurfuryl alcohol [102] and glycerol [92, 103] hydrogenolysis. Another study using Rh- ReO_x /C for hydrogenolysis of cyclic ethers did both experimental and computational studies to propose that this increase in selectivity to C-O bond scission at the more sterically hindered carbon may be due to the ability of OH groups on ReO_x sites to stabilize the intermediate carbenium ions [96]. To illustrate this mechanism, Fig. 1.11 shows the proposed reactant and intermediate adsorption states for tetrahydrofurfuryl alcohol hydrogenolysis on Rh(111) modified with an Re-OH

site.

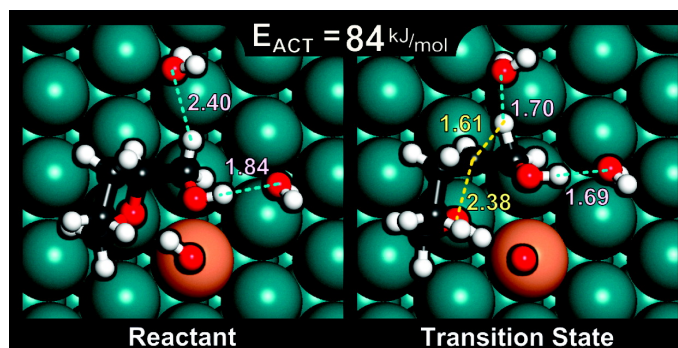


Figure 1.11: DFT-calculated reactant and transition state adsorption structures for tetrahydrofuryl alcohol hydrogenolysis. The mechanism is proposed to be a concerted protonation, hydride transfer, and ring opening over Re-OH modified Rh(111). From [96]

Increased hydrogenolysis selectivity has been observed for linear oxygenates as well [96]. Ir-ReO_x/SiO₂ showed higher selectivity to 1,4-butanediol production from erythritol hydrogenolysis than unmodified Ir [104]. This increase in selectivity from 0% to 33% was again proposed to be due to formation of an alkoxide species on ReO_x sites followed by hydrogenolysis by a hydride species on a neighboring Ir site. Similar results were found for glycerol hydrogenolysis on Ir-ReO_x/SiO₂, with increased C-O scission attributed to formation of an alkoxide [105–107]. Characterization work on Ir-ReO_x surfaces has supported this hypothesis that interaction between the two sites is important in the enhanced hydrogenolysis; a combination of XAS, TPR, XPS, and CO chemisorption suggested that there is significant interaction between the Ir sites and the low valent ReO_x [108]. A similar investigation for Rh-ReO_x also found that the two sites were well mixed and interacting [109].

1.4 Thesis goals

The overall goal of this thesis is to gain a more fundamental understanding of the role of oxophilic metal modifiers in bimetallic catalysts in increasing deoxygenation activity and selectivity. These catalysts (for example, noble metals modified with Re or Mo) have been shown to be promising catalysts, yet the precise role of the oxophilic metal is still debated. Surface science

experiments were conducted to investigate structure-property relations of these catalysts, using Mo/Pt(111) as a model catalyst surface, as well as to probe reaction mechanisms of pyrolysis oil model compounds. These results were used to support hypotheses formed from experiments using supported PtMo catalysts. The insight gained from these experiments may be used to design improved supported bimetallic catalysts for biomass deoxygenation applications.

1.5 Thesis organization

Chapter 2 of this thesis is dedicated to better understanding structure-property relations for Mo-modified Pt(111). Supported catalysts can be difficult to systematically investigate due to the heterogeneous surface structure; the variation of surface sites often complicates gaining molecular level understanding of reaction mechanisms. Using a single crystal under ultra-high vacuum (UHV) conditions helps eliminate some of these variables. The adsorption of important small molecules including H_2 , CO, and water were studied through temperature-programmed desorption (TPD). The interaction of the bimetallic surface with O_2 and the influence of the oxophilic metal's oxidation state on reactivity were also investigated experimentally through TPD and X-ray photoelectron spectroscopy (XPS), as well as computationally using density functional theory (DFT).

Chapter 3 focuses on extending this understanding of the Pt-Mo system to the deoxygenation mechanism of complex oxygenates using a combination of UHV studies, computation, and upgrading experiments with supported catalysts. Benzyl alcohol ($\text{C}_6\text{H}_5\text{CH}_2\text{OH}$) was used as a probe molecule for the lignin-derived portion of pyrolysis oil. The mechanism of benzyl alcohol decomposition was investigated on Mo-modified Pt(111) and the results were extended to supported nanoparticle catalysts. DFT calculations were also performed to further investigate the influence of oxophilic modifiers on adsorption of aromatic reactants. 2-Methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$) was also studied under UHV conditions to probe the importance of the aromatic ring on the modifier's enhancement of deoxygenation selectivity.

Chapter 4 reports on a detailed investigation the role of Mo on the deoxygenation mechanism of m-cresol ($\text{C}_6\text{H}_5\text{CH}_3\text{OH}$). This phenolic compound is often studied as a model compound for

pyrolysis oil but the mechanism for deoxygenation over noble metal-based catalysts is still debated. Through upgrading experiments on supported catalysts along with DFT calculations the mechanism for the increased deoxygenation selectivity over PtMo catalysts was investigated.

Chapter 5 uses the insight gained throughout the rest of the thesis work to identify a design strategy for improved deoxygenation catalysts. The results detailed in chapters 2-4 suggested that oxophilic/noble metal combinations that form strong metal-oxygen bonds and weak metal-carbon bonds may be ideal. Through DFT calculations various bimetallic catalysts were screened and promising combinations were tested in preliminary screens of deoxygenation performance.

Finally, chapter 6 summarizes the work performed in the previous chapters and concludes with final thoughts on the role of oxophilic metal modifiers for deoxygenation catalysts. It also discusses how catalysts can be further improved to advance the feasibility of making biomass-derived fuels and chemicals.

Chapter 2

Interactions of hydrogen, carbon monoxide, oxygen, and water with molybdenum-modified platinum(111)

Modification of platinum group catalysts by molybdenum is known to improve catalyst performance in a number of important chemical reactions. To investigate fundamental mechanisms responsible for the promoting effect of Mo, temperature-programmed desorption (TPD) and low energy electron diffraction (LEED) experiments were performed to examine the adsorption of O₂, D₂, CO, and H₂O on Pt(111) modified with submonolayer quantities of Mo. Auger electron spectroscopy (AES) was used to detect and quantify the Mo coverage and X-ray photoelectron spectroscopy (XPS) was employed in conjunction with density functional theory (DFT) calculations to identify Mo species present following various surface treatments. The state of Mo on the surface was found to vary depending on prior surface treatment. Treatment with O₂ resulted in a surface Mo oxide, whereas treatment with H₂ resulted in a reduced bimetallic surface. XPS results indicate that high pressures of O₂ create a higher valent oxide than what is created under ultrahigh vacuum. Oxidized Mo appeared to block Pt surface sites without significantly altering the behavior of species adsorbed on Pt. Reduced surfaces, on the other hand, were shown to decrease yield and desorption temperature for both D₂ and CO. Isotopic TPD studies provided evidence of H₂O dissociation on the reduced Mo modified surface, with a maximum extent of H₂O dissociation occurring at intermediate Mo coverages.

2.1 Introduction

Bimetallic catalysts consisting of a platinum group element and an oxophilic metal such as Re or Mo have received a great deal of attention for their ability to selectively break C-O bonds as well as resist CO poisoning [35, 93, 96, 97, 99, 110]. This makes them attractive materials for upgrading the highly oxygenated compounds derived from gasification or pyrolysis of biomass, as well as for CO-tolerant fuel cell anodes. The presence of these two metals can result in both facile H₂ activation as well as weak H binding to the surface, which is particularly desirable for hydrogen fuel cell applications [111]. Despite the wide range of studies that have been performed, there is still debate over the role of the oxophilic modifier in these systems. One hypothesis is that H₂O is able to dissociate on the bimetallic surface and create Brønsted acid sites; the oxophilicity of the modifier sites allows them to be hydroxylated with a strong metal-O bond weakening the O-H bond [35, 93, 97, 99].

In this contribution we report on the use of temperature-programmed desorption (TPD), low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS) up to elevated pressures (about 133 Pa) to investigate how Mo addition to Pt(111) influences adsorption of key gases such as O₂, H₂ (or D₂), CO, and H₂O. Understanding how the bimetallic surface interacts with these molecules is critical in designing optimal fuel cell anodes and catalysts for use in biomass upgrading. Both of these applications are often hindered by CO poisoning and take place in H₂- and H₂O-rich environments. The majority of previous work has been conducted on supported catalysts or electrodes under high-pressure conditions, making it difficult to develop a detailed understanding of the role of the modifier on surface reaction mechanisms. Here we aim to provide a more fundamental understanding of the PtMo surface by studying a model system under ultrahigh vacuum (UHV) conditions. TPD was used to provide insight into the adsorption energies of these small molecules on the bimetallic surfaces and LEED allowed investigation of their structure and order. XPS was used to assign Mo oxidation states to further characterize the modified surfaces. The results indicate that the oxidation state of the

modifying Mo plays a strong role in the surface chemistry.

2.2 Experimental and computational methods

All TPD, LEED, and AES experiments were performed under ultrahigh vacuum in a chamber described previously [112]. The chamber has a base pressure of about 1.3×10^{-7} Pa and is equipped with a Smart- IQ+ quadrupole mass spectrometer (VG Scienta) as well as a combined LEED/AES apparatus (Series RVL 2000, LK Technologies). An electron gun mounted on the same flange as the reverse view LEED screen was used for both LEED and AES. A cylindrical mirror analyzer (CMA; Model CMA 2000, LK Technologies) oriented at a 90° angle to the electron gun was used to detect Auger electrons. The Pt(111) sample (Princeton Scientific) was mounted on a 1.5 mm tantalum disk that was held onto a copper stage by metal clips. Isotopically labeled H_2O , $^{18}\text{OH}_2$ (97 atom %, Aldrich), was dosed onto the surface using a direct dosing line pointed at the sample. CO (99.9% purity, Matheson Trigas), D_2 (99.96 atom %, Isotec), and O_2 (ultrahigh purity, AirGas) were dosed indirectly in Langmuirs (L). When dosing in Langmuirs the chamber was filled to the required pressure with the adsorbate of interest to allow 100 s of dosing time. For example, to dose 5L CO, the chamber pressure was held at 5×10^{-8} Torr (or 6.7×10^{-6} Pa) for 100 s. The sample was cooled through thermal contact with a liquid nitrogen reservoir. The temperature was measured by a thermocouple welded next to the sample on the stage. When using the Redhead equation [113] to calculate activation energies based on peak desorption temperatures, a pre-exponential factor of 10^{13} s^{-1} was assumed.

Mild cleaning was performed through heating and cooling cycles between 400 and 1000 K in 6.7×10^{-6} Pa O_2 . Mo was removed from the sample using a model NG13000-SE sputter gun (LK Technologies). A total of 6-8 sputter cycles were used consisting of 5 min of annealing at 800 K in 1.3×10^{-4} Pa O_2 , 5 min of annealing at 973 K, and 20 min of Ar^+ sputtering (2 keV) in 1.3×10^{-3} Pa Ar (ultrahigh purity, Matheson Trigas).

Mo was deposited onto the Pt(111) crystal by resistively heating a tungsten filament wrapped with a Mo wire (Strem Chemicals, 99.97%). The presence of Mo was confirmed using AES through

the growth of a Mo peak at 2.98×10^{-17} J. Due to the low intensity of this feature at small dose sizes, the Mo coverage was calculated using the attenuation of the Pt peak at 1.12×10^{-17} J [114, 115]. The Mo doser was operated for a range of times and the intensity of the 1.12×10^{-17} J Pt peak at each coverage was used to calculate film thickness. An uptake curve was constructed by plotting the film thickness as a function of dosing time. The resulting plot contains two distinct linear regions with different slopes; the break in the curve corresponds to the filling of the first monolayer [116]. The corresponding coverages are calculated to provide an estimation for the trend in how the amount of Mo deposited relates to the dosing time. The deposited Mo was oxidized at 800 K in 1.3×10^{-4} Pa O₂ and reduced at 800 K in 1.3×10^{-4} Pa H₂ (99.999% purity, AirGas).

To create the oxidized surfaces for the studies reported below the sample was held in O₂ at 800 K and then oxidation was confirmed through two sequential O₂ TPDs with the same peak intensity. To produce a reduced surface, the crystal was treated at 800 K in H₂ until an O₂ TPD showed no O₂ peak (15-30 min, depending on Mo coverage).

Ambient pressure XPS (AP-XPS) experiments were performed at Brookhaven National Laboratory at beamline X1A1 at the National Synchrotron Light Source (NSLS). This system has been described in detail elsewhere [117]. The sample was held >0.5 mm away from the 500 μ m entrance aperture of the electron analyzer. The temperature was measured with a type K thermocouple spot-welded to a tantalum backplate located between the heater and crystal. A differentially pumped hemispherical analyzer (Specs Phoibos 150 NAP) was positioned 70° from the incident X-ray beam and 20 degrees from the surface normal of the sample. Mo 3d and Au 4f reference spectra (measured on a Au foil adjacent to the Pt crystal) were collected at a photon energy of 9.08×10^{-17} J. The Pt(111) sample was cleaned by Ar⁺ sputtering and annealing. Mo was deposited onto the Pt(111) sample using an electron beam evaporator (Specs EBE-1) and a 2.0 mm Mo wire (Alfa Aesar, 99.95%). Coverage was approximated using the Pt 4f peak attenuation by calculating the mean free path of an electron through a monolayer of Mo and estimating the reduction in Pt 4f intensity expected.

XPS analysis was performed using OriginPro 9 (OriginLab Corporation) for peak deconvolution. A gold foil reference was used to determine binding energies relative to Au $4f_{7/2}$ at 1.35×10^{-17} J. Baseline subtractions were done using the Shirley method [118]. Peaks were fit using the sum form of a pseudo-Voigt function that is 20% Lorentzian and 80% Gaussian. All peaks have both Gaussian and Lorentzian contributions with a full width and half maximum (fwhm) of $2.56 \times 10^{-19} \pm 3.20 \times 10^{-20}$ J. The Mo $3d_{5/2}$ and $3d_{3/2}$ peaks were separated by $4.81 \times 10^{-19} \pm 1.60 \times 10^{-20}$ J and the $3d_{5/2}/3d_{3/2}$ area ratio was held at 3:2 [119]. The area under each of the deconvoluted peaks was also calculated in Origin and used to estimate the yield of each species after the various treatments. The contribution of each oxidation state on the surface composition was approximated by rounding to the nearest 5%.

The Vienna Ab Initio Simulation Package (VASP) was used to perform density functional theory (DFT) calculations. The plane-wave basis set was cut off at $2.56 \times 10^{-19} \pm 6.34 \times 10^{-17}$ J and the projector-augmented wave method was used for the core electrons [120, 121]. The k-point mesh was $7 \times 7 \times 1$ for the geometric relaxations, and was increased to $13 \times 13 \times 1$ for the binding energy shift calculations. A 3×3 surface cell with four layers was used, with the bottom two layers fixed in their bulk positions while the top two layers were relaxed. Various Pt atoms in the top two layers of a Pt(111) surface were replaced with Mo atoms to give different models of a PtMo alloy.

Electron binding energy shifts were calculated relative to Mo(110) using the initial state approximation, meaning that the effect of ionization was not accounted for. Although including final state effects increases the accuracy of the shifts, the initial state approximation has been shown to accurately capture trends in close-packed transition metal alloy surfaces [122, 123]. Binding energies and shifts were calculated relative to the Fermi level.

2.3 Results

2.3.1 Surface chemistry of oxygen

LEED patterns were collected for the Pt(111) surface both before and after Mo deposition. The clean Pt(111) surface showed the expected sharp (1×1) pattern, shown in Fig. 2.1a [116]. Fig. 2.1b shows LEED images taken for about 0.25 ML of Mo on Pt(111). Consistently across submonolayer Mo coverages the Mo-modified surface showed two clearly resolved spots. The appearance of a second spot within a LEED pattern is typically attributed to the presence of step edges [124]. However, in this case it suggests the presence of additional adatoms of Mo on the Pt surface. Doubling of LEED spots has been observed in other bimetallic systems and has been attributed to contributions of the two metals that are present in the first several surface layers to the overall diffraction pattern [125]. In the present study, the reduced surface remains ordered enough to observe this doubling effect.

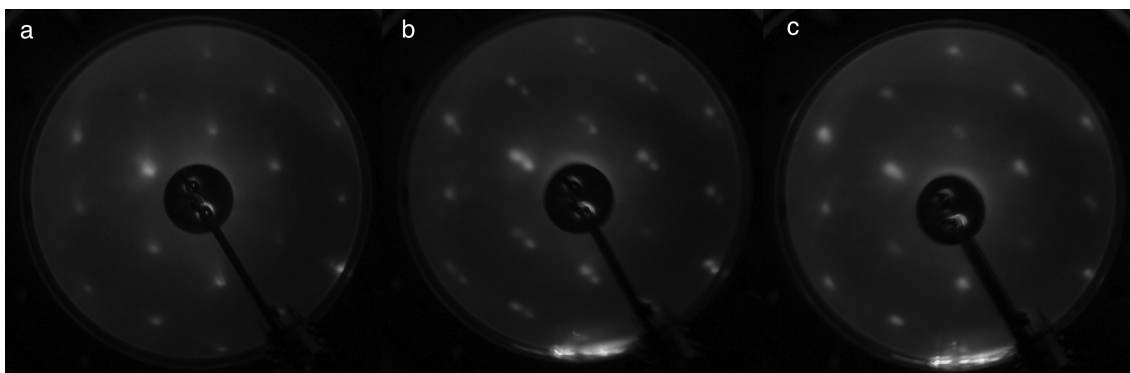


Figure 2.1: LEED patterns at 3.17×10^{-17} J for (a) Pt(111), (b) reduced 0.25 ML Mo/Pt(111), and (c) oxidized 0.25 ML Mo/Pt(111).

O₂ TPD was used to investigate the surface chemistry of O on the Mo-modified Pt(111) surface. Because Mo is an oxophilic metal, we hypothesized that formation of a surface oxide would occur during these experiments. The Mo was confirmed to be oxidized through repeated O₂ TPDs using the mild cleaning procedure described in the experimental methods section (Fig. 2.2). On a freshly reduced surface, O₂ TPD showed no O₂ peak (shown by the spectrum labeled “Reduced

Surface” in Fig. 2.2). This indicates that the surface had been reduced and all of the O_2 was being used to create the oxide. Subsequent TPDs yielded a higher O_2 intensity than the previous ones as more of the Mo became oxidized and less of the dosed O_2 was taken up by the Mo. The surface was judged to be fully oxidized when successive TPDs had the same O_2 intensity. When this procedure was repeated for a higher coverage of Mo a greater number of O_2 cycles was required and the final intensity of the saturated O_2 peak was lower.

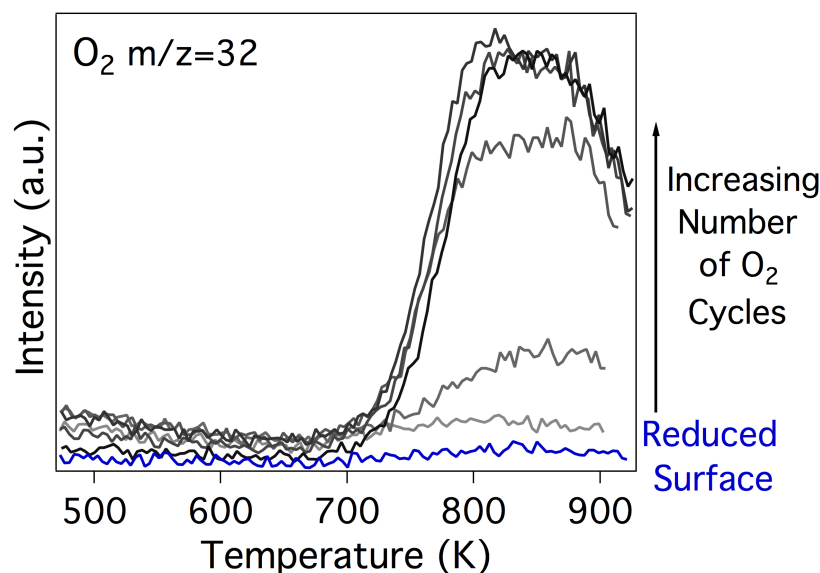


Figure 2.2: Repeated O_2 TPDs used to confirm oxidation on 0.15 ML Mo/Pt(111). Each cycle consists of cooling the surface in O_2 as described in the experimental procedures then ramping the temperature. The first cycle is shown with the lightest shade of gray and subsequent cycles are shown with increasingly dark lines.

Fig. 2.1c shows the LEED pattern obtained for the same surface seen in Fig. 2.1b after oxidation. The doubling observed for the reduced surfaces is no longer present. Instead, the pattern is made of single spots that are less sharp than on a clean Pt surface. This suggests that the oxidized surface is less well ordered. In order to see a clear diffraction pattern the surface atoms must be well ordered; the blurred spots seen for the oxidized surface may indicate that there is no longer a pristine (111) surface.

XPS was used to further characterize these oxidized and reduced surfaces. Approximately

0.4 ML Mo was deposited onto the Pt(111) crystal. Spectra were recorded for the surface after deposition, after subsequent annealing to 800 K, and after oxidation or reduction for 30 min at 800 K. The oxidation and reduction procedures used for the TPD experiments reported here were carried out. Additionally, the same procedure was performed by in situ AP-XPS in 80 Pa of O₂ or H₂ to study the surface under conditions closer to those associated with heterogeneous catalysis. Resulting spectra are shown in Fig. 2.3. After oxidation in 2.7×10^{-5} Pa O₂ the peaks shift to 1.60×10^{-19} J higher binding energy. Oxidation in 80 Pa O₂ caused a shift of nearly 4.01×10^{-19} J to higher binding energy relative to the peaks of the freshly prepared surface. Reduction in both 2.7×10^{-5} and 80 Pa of H₂ shifted the peaks back to within 1.60×10^{-20} J of their initial position after deposition.

The results of deconvoluting the Mo 3d peak for oxidation state assignments can be seen in Table 2.1. By deconvoluting the raw Mo3d peaks as described in the experimental methods section the peak positions for each Mo species could be estimated. As deposited, the surface contains primarily Pt-Mo sites, defined as Mo atoms with a higher binding energy than pure metallic Mo due to interaction with Pt neighbors. There is also a small amount of oxidized Mo present after deposition, likely caused by background O₂ interacting with the surface. A small O 1s feature was observed on the surface after deposition. After annealing at 800 K, a small peak could be fit at 3.66×10^{-17} J that corresponds to metallic Mo. The subsequent oxidation procedures formed a mixture of oxides. Both reduction treatments created similar surfaces, with the majority of the Mo being in Pt-Mo and a small amount of oxide still present as well. Mo⁺⁴ corresponds to MoO₂ and Mo⁺⁶ corresponds to MoO₃. The assignment of Mo⁺⁵ likely arises from a partially reduced MoO₃.

Table 2.1: Binding Energy Assignments for Oxidation States of Mo 3d_{5/2} Calculated by Deconvolution of Mo 3d XP Spectra^a

Oxidation state	Binding energy (J $\times 10^{-17}$)
metallic	3.656 ± 0.002
Pt-Mo	3.666 ± 0.002
+4	3.681 ± 0.002
+5	3.704 ± 0.003
+6	3.739 ± 0.002
^a All binding energies referenced to Au 4f _{7/2} = 1.35×10^{-17} J	

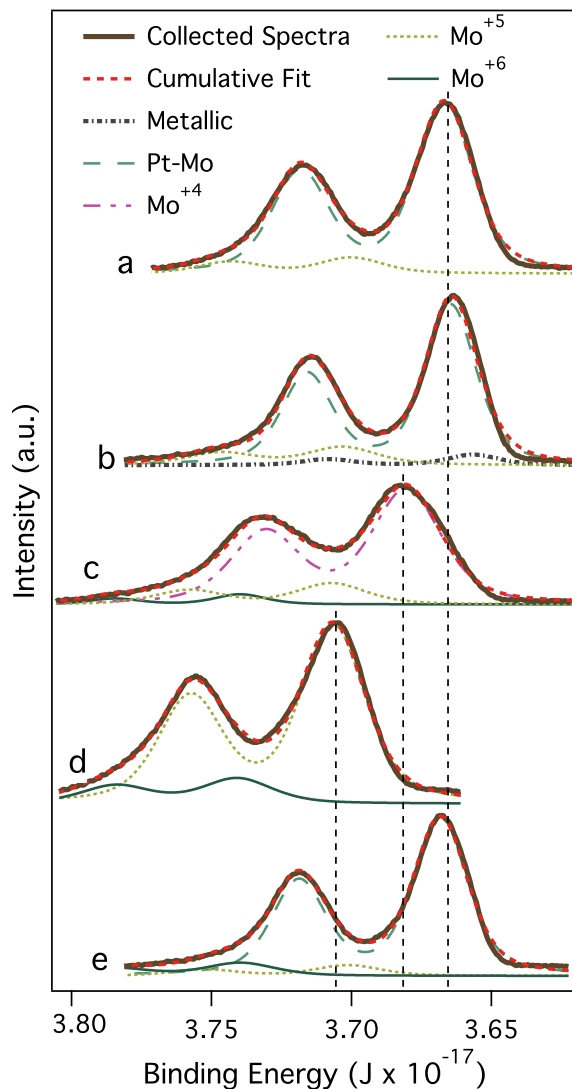


Figure 2.3: XP spectra for Mo3d peaks of approximately 0.4 ML Mo/ Pt(111) (a) as deposited and (b) after annealing 30 min at 800 K; and after treatment at 800 K for 30 min in (c) 2.7×10^{-5} Pa O₂, (d) 80 Pa O₂, and (e) 2.7×10^{-5} Pa H₂. Binding energies referenced to Au 4f_{7/2} = 1.35×10^{-17} J.

To provide support for the assignment of the 3.666×10^{-17} J peak to Mo interacting with Pt neighbors, DFT was used to calculate electronic binding energy shifts of the 3d level of Mo in a variety of PtMo alloys, four of which can be seen in Fig. 2.4. By varying the local composition of the alloys, it was observed that the binding energy shift was sensitive to the number of Mo-Mo bonds. Isolated Mo atoms (i.e., those that are only bound to Pt atoms) are observed to have

binding energy shifts greater than 1.602×10^{-19} J compared to a Mo(100) surface. The magnitude of this shift decreases as Mo-Mo bonds are introduced.

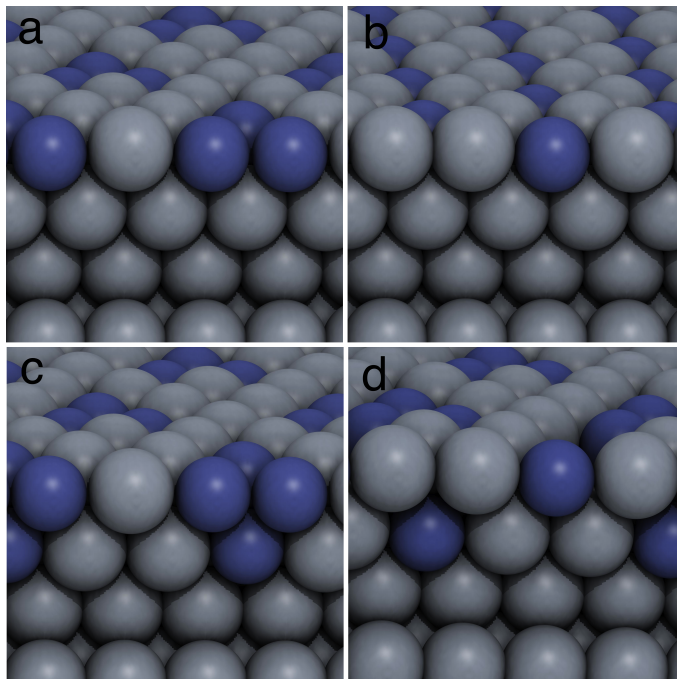


Figure 2.4: Selected surfaces used to model PtMo, with 1/3 ML Mo in the surface layer as (a, c, d) clusters (b) dispersed atoms. In (c) a subsurface Mo atom is below each Mo cluster, and in (d) subsurface Mo atoms are below Pt atoms.

The relationship between binding energy shift and number of nearest Mo neighbors is plotted in Fig. 2.5. As shown in the figure, the experimental binding energy shifts are consistent with a PtMo alloy where each Mo atom has 2 Mo nearest neighbors. Surface and subsurface Mo atoms would be very difficult to distinguish using binding energy shifts. Variations in binding energy shifts for the same number of Mo nearest neighbors can be attributed to Mo next-nearest neighbors, where more Mo next-nearest neighbors leads to a smaller shift. While these trends are too subtle to precisely identify the exact configuration of bimetallic surface sites, overall they are consistent with our assignment of Pt-Mo sites to a binding energy roughly 9.613×10^{-20} J higher than that observed for metallic Mo. It should also be noted that any of these numbers of nearest neighbors (from 0 to 6) is plausible experimentally; depending upon the dispersion of the Mo atoms various

cluster sizes may be expected.

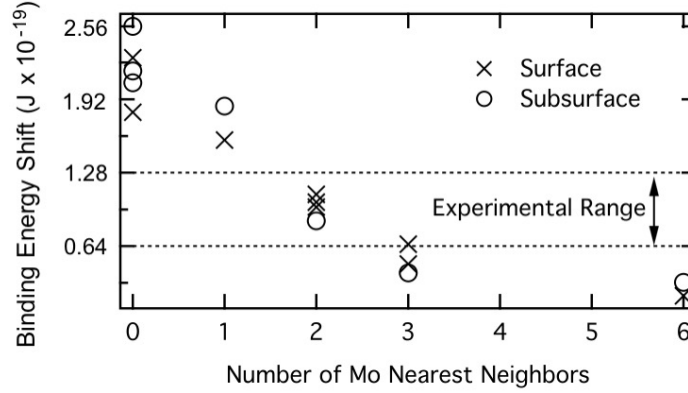


Figure 2.5: Binding energy shifts calculated with DFT, with the experimental range shown for reference.

The oxidation state assignments of Table 2.1 were used to estimate the composition of each surface studied by computing the area under each curve in the deconvolution. Table 2.2 shows the approximate percentages of each oxidation state under the various conditions tested. Based on these results, the TPDs performed in this study led to the presence of Mo^{4+} , Mo^{5+} , and Mo^{6+} for oxidized surfaces and Pt-Mo sites with some Mo^{5+} and Mo^{6+} still present for reduced surfaces. Treatment of the surface in higher O_2 pressure led to formation of higher valent oxides, possibly suggesting that formation of MoO_2 is favored in the low pressure range used in high vacuum studies.

Table 2.2: Approximate Percentages of Each Oxidation State in the Mo 3d XP Spectra after Each Treatment for approximately 0.4 ML Mo/ Pt(111)

	metallic	Pt-Mo	+4	+5	+6
as deposited		90		10	
annealed at 800 K	5	85		10	
oxidized in 2.7×10^{-5} Pa O_2			80	15	5
reduced in 2.7×10^{-5} Pa H_2		85		5	10
oxidized in 80 Pa O_2				85	15
reduced in 80 Pa H_2		85		10	5

Previous theoretical and experimental results for supported PtMo particles indicate the possibility of migration of reduced Mo into the bulk [126]. Evidence of diffusion of reduced Mo into the Pt(111) subsurface was seen when sputtering the sample. After Ar^+ sputtering and annealing

cycles were performed, initially no Mo could be detected by AES. However, after O₂ cleaning, the O₂ desorption temperature and peak shape began to shift toward that of a Mo covered surface. This no longer occurred when the sputtering procedure included an O₂ annealing step, suggesting that any Mo from the bulk had been drawn to the surface and was removed in the next sputtering cycle. XPS results also show evidence of migration. Fig. 2.6 shows XP spectra of the Mo 3d and Pt 4f regions taken after dosing approximately 0.6 ML Mo on Pt(111) and after annealing the surface to approximately 775 K. Heating the sample decreases the Mo intensity and increases the Pt, suggesting the surface layer is more Pt rich after annealing than initially after dosing.

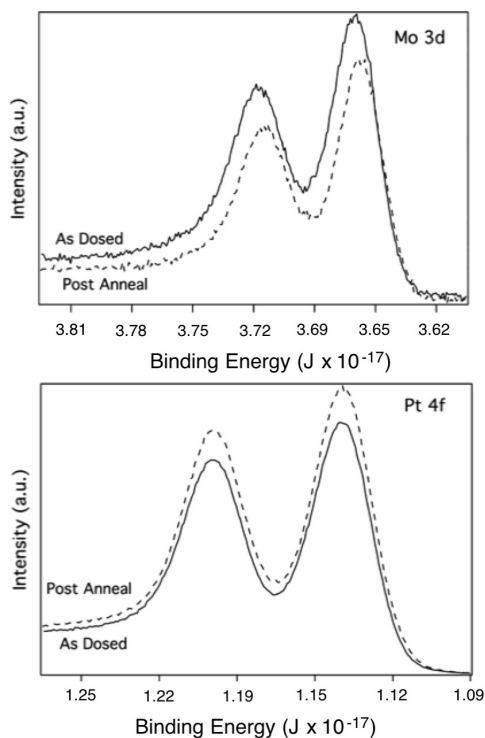


Figure 2.6: XP spectra of approximately 0.6 ML Mo/Pt(111) before (solid line) and after (dashed line) annealing.

The DFT energies of the various models of the PtMo surface were compared to give an idea of the most stable structures. These energies indicate that under vacuum, subsurface Mo is more stable than surface Mo by about 1.923×10^{-19} J/atom. This energetic difference is approximately the same for several different Mo structures and coverages. Previous computational studies have

found this as well; in both CO and H₂ environments Mo was found to migrate subsurface rather than forming an overlayer [111, 127]. Dispersed Mo atoms are generally more favorable than clustered Mo atoms. For example, a cluster of 3 Mo atoms (Fig. 2.4a) is less stable than the dispersed atoms (Fig. 2.4b) by about 3.525×10^{-20} J/atom, regardless of whether the Mo atoms are in the surface layer or the subsurface layer. The exception is that a subsurface Mo atom is more stable under a cluster of Mo atoms (Fig. 2.4c) than under Pt atoms (Fig. 2.4d) by about 1.282×10^{-20} J. Calculations of barriers for diffusion of Mo into the Pt bulk, which would be required to model the migration of Mo in detail, were beyond the scope of this work.

2.3.2 Carbon monoxide

The influence of Mo loading on the surface's interaction with CO was studied for both reduced and oxidized surfaces. The spectra in Fig. 2.7a from oxidized surfaces show decreasing CO yield as the Mo loading increases, despite initially exposing all surfaces to the same amount of CO. However, the desorption temperature remains approximately the same on all surfaces. The same trend was observed for H₂O dosed onto the oxidized surfaces. This suggests that the oxidized Mo is creating a disordered and inert layer on the Pt, blocking surface sites without influencing the electronic structure of the Pt. The high temperature shoulder on the spectrum from Pt(111) is consistent with past CO TPD experiments and has been attributed to desorption from either the sample holder or from defect sites [128]. The suppression of this feature when the Mo has been oxidized suggests that it results from defects which are covered by a MoO_x surface species. Due to the TPD evidence along with LEED results indicating that oxidized Mo creates a disordered surface species that does not influence the behavior of the adsorbates or the Pt, the remainder of the TPD studies presented here were performed on reduced surfaces.

Fig. 2.7b shows TPD spectra for a variety of Mo coverages that had been reduced prior to exposure to 5L of CO at 373 K. Increasing Mo coverage reduced both the yield and desorption temperature of CO. The lower desorption temperatures are not explained by CO desorption from metallic Mo alone; on a Mo(100) surface molecularly adsorbed CO is expected to desorb near 400

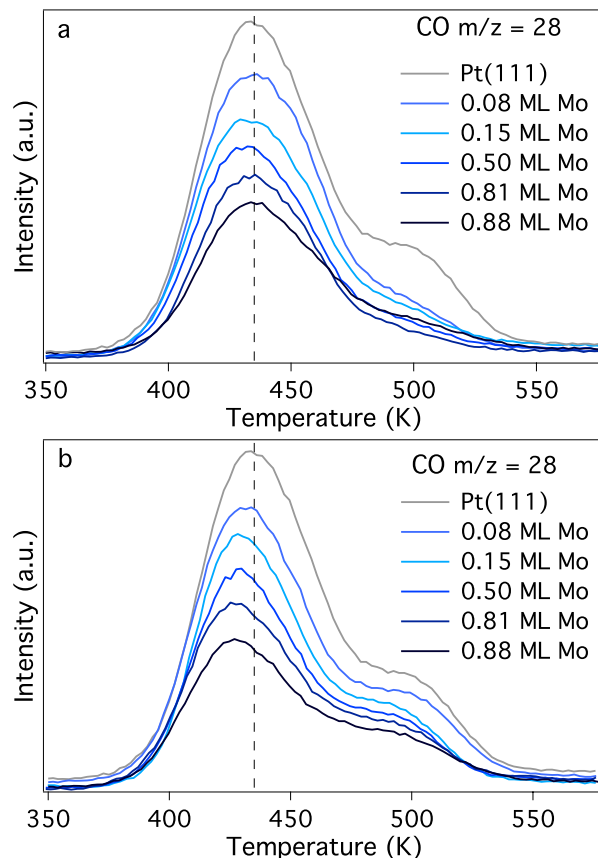


Figure 2.7: Spectra of 5L CO on (a) oxidized and (b) reduced surfaces of increasing Mo coverage.

K [129]. CO dissociative adsorption is also observed on Mo(100), with recombinative desorption occurring between 900 and 1240 K [129]. No evidence of CO dissociation was found on any of the Mo/Pt(111) surfaces: post-TPD AES spectra showed no formation of carbon features and the high temperature CO recombination peaks were not observed.

2.3.3 Deuterium

Fig. 2.8 shows D_2 TPDs performed on reduced Mo/Pt(111) surfaces with varying Mo coverages. Each TPD was performed following a 3L dose of D_2 at 223 K. As was seen for CO on reduced surfaces, with increasing Mo coverage both the desorption temperature and the yield of D_2 decreases. The observed desorption temperature on Pt(111) of 320 K is consistent with what

has previously been observed for a high coverage of H [130]. The desorption temperature of 290 K for 0.88 ML Mo/Pt(111) is close to the desorption temperature of H₂ on Mo(100) [129]. Note that there is a large temperature shift for H₂ desorption even at very low Mo coverages (e.g., 0.08 ML), suggesting that Mo has a significant electronic effect on Pt surface sites.

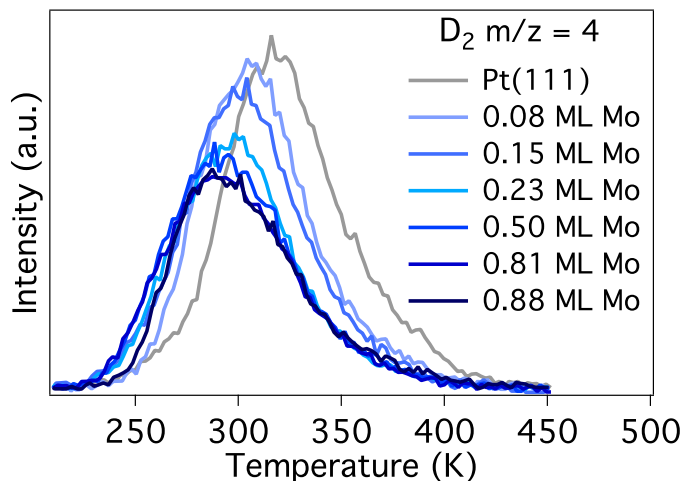


Figure 2.8: TPD spectrum following 3L D₂ exposure at 223 K on reduced surfaces of increasing Mo coverage.

2.3.4 Water

TPD studies were performed with isotopically labeled H₂O (¹⁸OH₂) to detect the possible dissociation of H₂O on the reduced Mo/Pt(111) surfaces. Each surface was first covered with 3L D₂ at 223 K and then a fixed direct dose of ¹⁸OH₂ at 130 K. If hydroxylated sites are being generated on the bimetallic surfaces some of the desorbing H₂O will have D incorporated. H₂O is not expected to dissociate on Pt alone [131]. Fig. 2.9b,c show that no ¹⁸OHD or ¹⁸OD₂ was produced from a clean Pt(111) surface. Upon addition of 0.08 ML of Mo these species begin to be generated.

The production of ¹⁸OHD and ¹⁸OD₂ goes through a maximum at 0.15 ML Mo, then begins to decline. The decreasing yield of these dissociation products at high Mo coverages indicates that both Pt and Mo sites are important in the ability to create surface hydroxyls. This can be seen by comparing the relative peak intensities of ¹⁸OH₂ for each surface with the corresponding

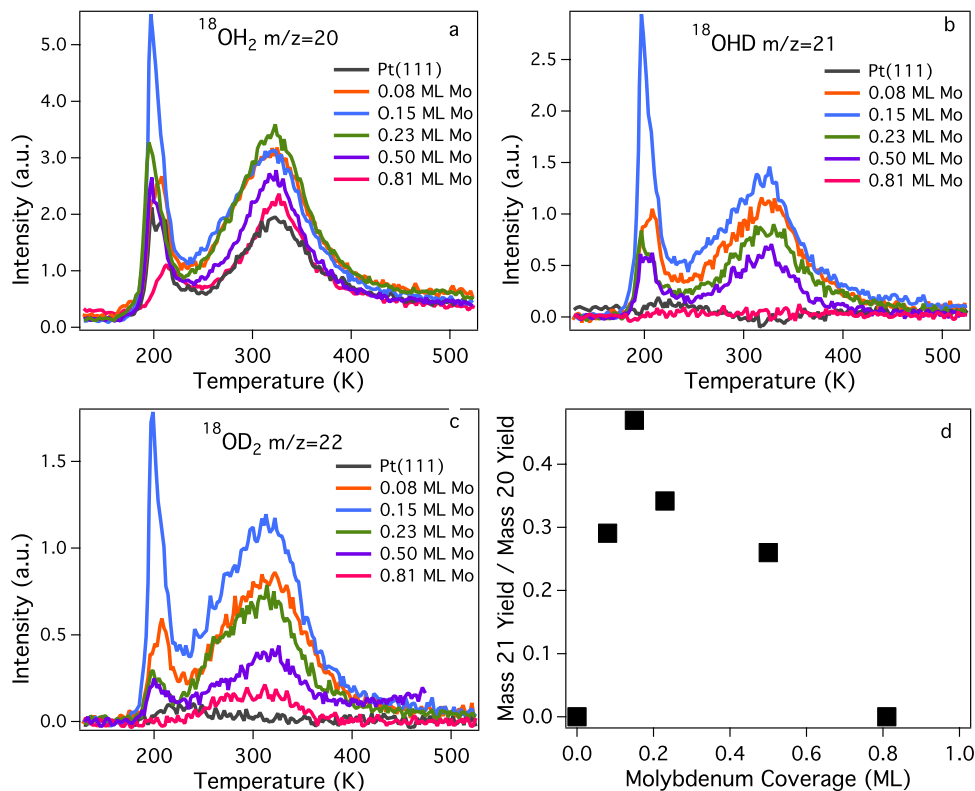


Figure 2.9: TPD spectra from dosing 3L D_2 with the dose of $^{18}\text{OH}_2$ shown (a) resulting in production of ^{18}OHD (b) and $^{18}\text{OD}_2$ (c). (d) Plot of ^{18}OHD yield normalized to $^{18}\text{OH}_2$ yield as a function of Mo coverage.

intensities of ^{18}OHD and $^{18}\text{OD}_2$. This trend can also be observed in Fig. 2.9d, which shows the approximate yield of ^{18}OHD with respect to the amount of $^{18}\text{OH}_2$ desorbed. Yields were estimated by integrating the TPD peaks for each surface tested. This suggests that both Pt and Mo sites are necessary to allow reversible dissociation to occur, making it possible to create hydroxyl groups on the surface.

2.4 Discussion

Oxophilic metals including Mo and its neighbor on the periodic table, Re, have been used as promoters of supported Pt group catalysts for key reactions. These include selective C-O bond hydrogenolysis in oxygenates derived from biomass [35, 96, 97, 99, 110] as well as improved

reforming catalysts⁴ and fuel cell anodes [111, 126, 132], all of which are inhibited by CO poisoning.

The XPS results reported here indicate that Mo is present in five states: metallic Mo, Mo interacting with Pt sites, as well as Mo in +4, +5, and +6 oxidation states. This is consistent with previously reported oxidation states for Mo foils and oxides [133–135]. DFT calculations suggest that the peak shifted to approximately 9.613×10^{-20} J higher binding energy than metallic Mo is consistent with Pt-Mo interactions. Previous computational and experimental results have identified the presence of a PtMo alloy, with Mo atoms able to fit into the Pt lattice [111, 136, 137]. While assignment of the feature to a low valent oxide cannot be ruled out [133, 134], previous XPS reports of PtMo alloy formation have shown binding energy shifts of 8.011×10^{-20} - 1.442×10^{-19} J [132, 138]. After annealing to 800 K a peak was found at 3.656×10^{-17} J, indicative of metallic Mo [119]. This suggests that upon annealing the Mo can continue migrating within the Pt surface layers and form additional Mo-Mo bonds, creating a small population of Mo sites that are not experiencing a strong interaction with Pt.

These oxidation state assignments indicate that the UHV O₂ treatment used in the TPD studies creates a surface that is primarily Mo⁴⁺. After the H₂ treatment used for TPD studies the surface is primarily Pt-Mo, with a small population of oxides still present. These Pt-Mo sites are likely the active site for interactions with small molecules. Using a higher pressure of O₂ to simulate conditions typical of heterogeneous catalysis formed more of the higher valent oxides, with the primary species being Mo⁵⁺. In a high-pressure reducing environment the Mo would be in a form similar to the surface formed for UHV reduction conditions.

When O₂ is present 3d metals have been shown both experimentally and in DFT calculations to migrate to the surface [87, 139]. Mo appears to behave similarly, with its oxophilicity driving out any subsurface metal when O₂ is introduced to create an oxidized surface layer. The influence of oxidized Mo on CO desorption is consistent with previous experimental results using MoO₃/Al₂O₃ catalysts; CO TPD spectra showed peaks at the same temperature as on pure Al₂O₃ with reduced CO adsorption as the MoO₃ loading was increased [140]. The formation of a surface oxide which solely acts to decrease the available number of CO binding sites has been seen previously when

studying SiO_x on $\text{Pd}(111)$ and $\text{Pt}(111)$ [112, 141]. In this case, addition of an annealed SiO_x layer to the surface left the CO desorption peak shape unaffected while substantially reducing the yield, suggesting a site-blocking effect by the oxide analogous to what was observed for MoO_x .

Unlike the oxidized surface, reduced Mo appears to have a significant electronic effect on the Pt. The lower CO desorption temperature on reduced surfaces agrees with computational predictions that oxophilic metal modifiers improve catalyst performance in part by reducing the CO binding strength on Pt sites [111, 136, 142]. If the CO desorption energy is an atomic property of a given site, as proposed by Hammer et al., it is dictated by the location of the d-band center [143]. In the case of bimetallic systems, addition of a second metal such as Re or Mo has been shown to decrease the Pt d-band center, thus, decreasing the CO desorption energy [87, 111, 142, 143]. Our calculations also indicate that Pt's binding energy shifts downward upon alloying with Mo, and this is expected to correlate with d- band center shifts [144]. The observed CO desorption peak temperatures were used to estimate the adsorption energy on the given surface using Redhead's equation [113]. The adsorption energy of CO on clean $\text{Pt}(111)$ was calculated to be 118 kJ/mol, in good agreement with literature values [128]. Upon addition of 0.08 ML Mo, the CO desorption peak temperature shifts 5 K, lowering the calculated adsorption energy to 116 kJ/mol. After depositing 0.88 ML of Mo the CO desorption temperature had shifted 10 K lower and the adsorption energy had decreased to 115 kJ/mol. This agrees well with computational results for a PtMo system modeled with 1 ML of Mo that has migrated into the second layer; the CO binding energy was calculated to be about 114 kJ/mol [111].

The electronic effects of Mo on Pt can also be seen in the results of D_2 TPDs. The decrease in D_2 yield with Mo coverage suggests that Pt, which is known to be an effective hydrogenation catalyst [145], is responsible for allowing the D_2 to adsorb onto the surface. As a result, higher Mo loadings result in fewer available Pt sites and therefore lower D_2 yields from the same initial exposure. Mo, either directly in the surface layer or indirectly in the subsurface, creates lower temperature desorption sites due to its weaker interaction with H_2 . This significant influence on Pt-H bond strength can be seen upon addition of even very low coverages of Mo; with only 0.08 ML on the

surface the desorption temperature decreased from 320 to 305 K. As the availability of Mo-influenced sites increases, the overall desorption temperature shifts toward that of a Mo surface. This is consistent with previous DFT and TPD results for bimetallic surfaces. A computational study of a wide range of bimetallic surfaces, including PtMo, showed decreased H binding energy compared to the two pure metals [127]. A subsurface ML of Ni on Pt(111) showed both a decreased yield and desorption temperature of H₂ on the bimetallic surface compared to pure Pt(111), suggesting that a second species can weaken the metal-H bond strength even if it has migrated to the subsurface through electronically altering the Pt at the surface [87].

TPD results presented here indicate that when the Mo is reduced the resulting surface is active for dissociation of H₂O. ¹⁸OHD and ¹⁸OD₂ were produced on Mo/Pt(111) surfaces but not from Pt(111) alone. The presence of these species cannot be explained solely by exchange between adsorbed H₂O and surface D. Although exchange between H₂O and D₂O has been observed over Pt(111) due to hydrogen bonding between adsorbed H₂O molecules, adsorbed H on the surface was not shown to exchange with D₂O [146]. Adsorbed O on Pt(111) has been shown to promote H₂O dissociation and influence the desorption temperature, but the same trend has not been observed for a H covered surface [146]. When codosed, H₂O and H₂ both desorbed as they would when dosed individually, as observed here and in previous work for the unmodified Pt(111) surface [147].

H₂O dissociation on Mo modified Pt is consistent with past computational studies. A DFT study of H₂O on Pt₂Mo(111) calculated that despite being unfavorable on Pt(111) alone, H₂O dissociation on the bimetallic surface was nearly thermoneutral over the Mo sites [131, 142]. The surface hydroxyls formed in the process are expected to remain on Mo; on Pt₂Mo(111) the OH binding energy is calculated to be about 2.243×10^{-19} J stronger on Mo sites than on Pt [136]. This would leave Pt sites available to interact with oxygenates. While this surface structure is significantly different than the Mo-modified Pt(111) surface investigated here, the electronic effect resulting from formation of Pt-Mo sites may have a similar effect. As a result, the hypothesis that oxophilic modifiers on supported catalysts influence C-O bond scission by creating Brønsted acid sites to dehydrate neighboring oxygenates is possible [35, 93, 96, 97].

2.5 Conclusions

After oxidation, Mo deposited on Pt(111) appears to create a disordered and inert surface layer that blocks available sites. When the deposited Mo is reduced, LEED images indicate that the surface remains ordered with a doubling of the observed spots resulting from the presence of two metals in the surface layers. XPS and DFT results indicate that the main Mo species present after reduction is Pt-Mo. This reduced surface lowers both the yield and desorption temperature of D_2 , indicating that Pt is primarily responsible for D_2 activation but the Mo can weaken the binding energy to allow easier desorption. Reduced Mo was also seen to lower the yield and desorption temperature of CO, which is consistent with computational studies. ^{18}OHD and $^{18}OD_2$ were produced from Mo/Pt(111) that had been precovered with D_2 , providing evidence of H_2O dissociation in the presence of Mo.

Chapter 3

Surface chemistry of aromatic reactants on Pt and Mo-modified Pt catalysts

Supported catalysts containing an oxophilic metal such as Mo and a noble metal such as Pt have shown promising activity and selectivity for deoxygenation of biomass-derived compounds. Here, we report that PtMo catalysts also promote hydrogenolysis of the model compound benzyl alcohol over decarbonylation that is most prevalent over unmodified Pt. A combination of single crystal surface science studies, density functional theory (DFT) calculations, and vapor phase upgrading experiments using supported catalysts were carried out to better understand the mechanism by which Mo promoted deoxygenation. Mo was deposited in controlled, submonolayer quantities on a Pt(111) surface and reduced at high temperature. Temperature programmed desorption (TPD) experiments using benzyl alcohol as a reactant showed greatly enhanced yields of the deoxygenation product toluene at moderate Mo coverages. To understand how the interaction of the aromatic group with the surface influenced this reactivity, we investigated the adsorption of toluene as a probe molecule. We found that addition of Mo to Pt(111) significantly decreased the toluene adsorption strength. Density functional theory (DFT) calculations indicated that this decrease in adsorption energy was consistent with preferential incorporation of Mo into the subsurface. The DFT calculations showed that the weaker aromatic-surface interaction could lead to a tilted adsorption geometry for benzyl alcohol that promotes hydrogenolysis to toluene over decarbonylation to produce benzene and CO. In addition, incorporation of Mo, which leads to ring repulsion, aids in limiting the extent of decomposition of aromatic reactants over Pt surfaces. Alumina-supported Pt and PtMo catalysts were also tested for benzyl alcohol deoxygenation. PtMo

had a higher rate of toluene production and lower rates of benzene and benzaldehyde production. Additionally, when benzaldehyde was used as the reactant to measure decarbonylation activity the rate of benzene production was 2.5 times higher on Pt than PtMo. Overall, the results of temperature-programmed desorption (TPD), DFT, and supported catalyst experiments suggest that Mo modifier sites decrease aromatic ring binding to PtMo surfaces and improve selectivity to C-O bond scission.

3.1 Introduction

Lignocellulosic biomass is an attractive feedstock for the production of renewable fuels and chemicals. Conversion of energy crops and waste streams is possible through thermochemical routes, such as fast pyrolysis, which results in highly oxygenated liquid oils that must be upgraded in order to produce important platform chemicals. The pyrolysis oil consists of oxygenated aromatic compounds, due to the lignin decomposition, and the conversion of this oil depends on the ability to selectively break C-O bonds. Therefore, aromatic compounds, such as benzyl alcohol, may be informative in better understanding and identifying potential catalysts. Benzyl alcohol is a particularly informative probe molecule because unlike phenolic compounds, the C-O bond may be cleaved under ultra-high vacuum through decomposition on metal surfaces. This allows it to be studied in great detail using single crystal studies to elucidate reaction mechanisms, a task that is difficult using supported catalysts alone.

Bifunctional catalysts, in particular bimetallics, may be the most promising route for catalyzing the multiple reaction steps necessary to upgrade these multifunctional oxygenates. It has been shown that bimetallic catalysts that consisting of Pt group metals with oxophilic metals, such as Re, Mo, or Fe, have the ability to improve selectivity to C-O bond scission reactions [32, 50, 92, 96]. This may be due to the catalyst’s ability to alter both the adsorption strength and orientation of reactant molecules through an increased interaction with the oxygen containing functional group and a weaker binding of the carbon. This was seen by Shubina and Koper, where DFT studies showed that CO had weaker binding energies on a PtMo bimetallic than on pure Pt

surfaces, while OH had stronger binding energies when Mo was added [136].

Many studies of oxophilic promoters have been carried out for oxygenated aromatic compounds, and a key question for these reactions is how the promoter affects the interaction of phenyl groups with the surface. Here, we investigate the influence of Mo modification of Pt surfaces on the surface chemistry of aromatic reactants, including both benzyl alcohol and toluene. This study combined surface-level studies carried out on Mo/Pt(111) surfaces and density functional theory (DFT) calculations. Furthermore, to evaluate implications of these results for technical catalysts at high pressures, we carried out vapor phase upgrading experiments on Pt and PtMo supported on Al_2O_3 .

3.2 Methods

3.2.1 Experimental methods

All TPD experiments were performed under ultrahigh vacuum in a chamber described previously [112]. The chamber has a base pressure of about 1.3×10^{-7} Pa and is equipped with a Smart- IQ+ quadrupole mass spectrometer (VG Scienta) and a combined low energy electron diffraction (LEED)/Auger electron spectroscopy (AES) apparatus (Series RVL 2000, LK Technologies) with an electron gun mounted to the same flange as the LEED screen. A cylindrical mirror analyzer (Model CMA 2000, LK Technologies) oriented at a 90° angle to the electron gun was used to detect Auger electrons. The Pt(111) sample (Princeton Scientific) was mounted on tantalum foil spot welded to two tantalum filaments. The temperature was monitored by a thermocouple spot-welded between the sample and the tantalum foil backing. The sample was cooled through thermal contact with a liquid nitrogen reservoir. Isotopically labeled benzyl alcohol, benzyl alcohol- d_5 (CDN Isotopes) and toluene (Sigma Aldrich, anhydrous, 99.8%) were dosed onto the surface using a direct dosing line pointed at the sample.

Mo was deposited onto the Pt(111) crystal through resistive heating of a tungsten filament wrapped with a Mo wire (99.97%, Strem Chemicals). AES was used to quantify the coverage

of Mo as described previously [148]. Mild cleaning was performed through heating and cooling cycles between 400 and 773 K in 1.3×10^{-4} Pa O₂ (ultrahigh purity, AirGas). PtMo surfaces were reduced prior to TPD experiments at 773 K in 1.3×10^{-4} Pa hydrogen (99.999% purity, AirGas) as described and characterized in a previous report [148]. Mo was removed from the sample using a model NG13000-SE sputter gun (LK Technologies). A total of 8 sputter cycles were used consisting of 5 minutes of annealing at 773 K in 1.3×10^{-4} Pa O₂, 5 minutes of annealing at 773 K in vacuum, and 20 minutes of Ar⁺ sputtering (3.2×10^{-16} J) in 1.3×10^{-3} Pa Ar (ultrahigh purity, Matheson Trigas). Experiments on D precovered surfaces were exposed to 3L D₂ (99.96%, Isotec) at 223 K prior to benzyl alcohol-d₅ exposure.

Supported catalysts were prepared by incipient wetness impregnation of a porous γ -Al₂O₃ support (Albemarle MARTOXID AN/I, 150 m²/g BET surface area, 75- μ m particle diameters). Aqueous solutions were prepared of the metal precursors using chloroplatinic acid hexahydrate (Strem Chemical Inc.) and ammonium molybdate tetrahydrate (Strem Chemical Inc.). Pt/Al₂O₃ was prepared with a nominal loading of 5 wt%. PtMo/Al₂O₃ catalysts were prepared via co-impregnation of the two precursors with a 10:1 and 1:1 atomic ratio of Pt:Mo, containing the same amount of Pt with Mo added to create the desired composition at increased total metal loading. The catalysts were dried in air at 373 K then calcined for 2 h at 723 K in 50 sccm He and 30 sccm O₂. Characterization of these catalysts has been reported previously [9]. In addition, commercial 5 wt% Pt/Al₂O₃ (Sigma) was used for upgrading experiments, both as purchased and after depositing 1.5 wt% Mo via incipient wetness impregnation of the Pt catalyst. Under the reaction conditions used here an alumina blank showed no activity. Upgrading experiments were performed in an atmospheric pressure tubular packed bed flow reactor optimized for measuring kinetics at low conversion. Reactants were introduced by bubbling helium through the liquid compound that was immersed in a water bath at 326 K for benzyl alcohol and benzaldehyde or 308K for toluene. The saturated He was then mixed with H₂ and diluent He before flowing over the catalyst bed. The reactor effluent was analyzed using an Agilent Technologies 7890A gas chromatograph with a 30 m $\times$ 0.320 mm Agilent HP-5 (5% phenyl)-methylpolysiloxane capillary column and flame ionization

detector.

Carbon monoxide pulse chemisorption was performed to characterize active surface area and average particle size. Approximately 100 mg of catalyst was loaded into a Mircomeritics ChemiSorb 2720 and reduced in-situ at 673 K for 2 h in 40 sccm H_2 then purged in 20 sccm He for 15 h without exposure to air. CO chemisorption was then performed at 323 K using 1 mL injections of 10% CO in He. This temperature was chosen to ensure that any CO dosed would not adsorb onto the alumina surface [140] while remaining low enough to ensure no desorption would be expected from platinum [128], Mo [129], or Pt-Mo [148] sites. These injections were repeated until the intensity of the CO desorption peak remained constant within $\pm 0.5\%$, indicating that no additional CO was adsorbing.

Particle sizes were also measured using transmission electron microscopy (TEM) performed on an FEI Tecnai F-20 TEM operating at 200 kV. Particle size estimates were obtained using ImageJ software to analyze images, sampling at least 100 particles for each material.

3.2.2 Computational methods

The Vienna Ab Initio Simulation Package (VASP) [149, 150] was used to perform density functional theory (DFT) calculations. The plane-wave basis set was cut off at 6.345×10^{-17} J and the projector-augmented wave method was used for the core electrons [120, 121]. The k-point mesh was $7 \times 7 \times 1$ for the geometric relaxations. A 3×3 surface cell with four layers was used with various Pt atoms in the Pt(111) lattice replaced with Mo atoms to give different models of a PtMo bimetallic surface. Visualizations of these structures were generated using QuteMol [151]. The atoms were placed in the subsurface due to previous experimental and computational studies suggesting Mo prefers to migrate here when reduced [111, 126, 127, 148]. The structure of the Mo sites in each surface tested is shown in Fig. 3.1. One-atom clusters were formed using the atom labeled 1 in the various layers. A 3 atom cluster was modeled using atoms 1-3, 4 atom clusters using 1,2,3 and 5, and a monolayer contained all 9 atoms in the layer.

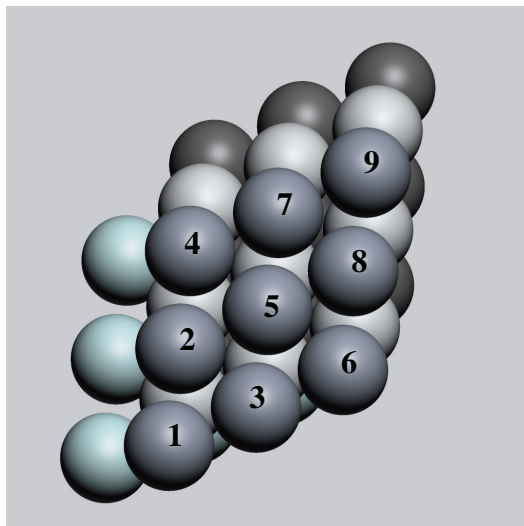


Figure 3.1: Orientation of Mo atoms within the Pt lattice in the surface models used in the present study. Differently shaded atoms represent different layers in the slab.

3.3 Results

3.3.1 Preparation of Mo-covered surfaces

Preparation and characterization of Mo-covered Pt(111) has been described previously [148], so only a brief summary is provided here. We deposited various Mo coverages on clean Pt(111) via evaporation through resistive heating of a Mo wire. The coverage of Mo was determined using AES after evaporation, prior to annealing the sample. The surfaces were then reduced by heating to 773 K in 1.3×10^{-4} Pa hydrogen. We previously found that this treatment allowed regeneration of a reduced surface following TPD experiments, such that the same Mo coverage and structure (as measured by AES, LEED, and XPS) was reproducible across experiments [148]. Our previous XPS studies were consistent with a model in which Mo at least partially diffused to a subsurface layer as a result of the pretreatment, shown by attenuation of the Mo peaks and increasing intensity of the Pt peaks between deposition and annealing. We further discuss this model below.

3.3.2 Benzyl alcohol TPD

Benzyl alcohol decomposition was studied on clean and Mo-modified Pt(111) surfaces. Fig. 3.2 shows the spectra of important mass fragments obtained from benzyl alcohol- d_5 ($C_6D_5CH_2OH$) exposure on various surfaces.

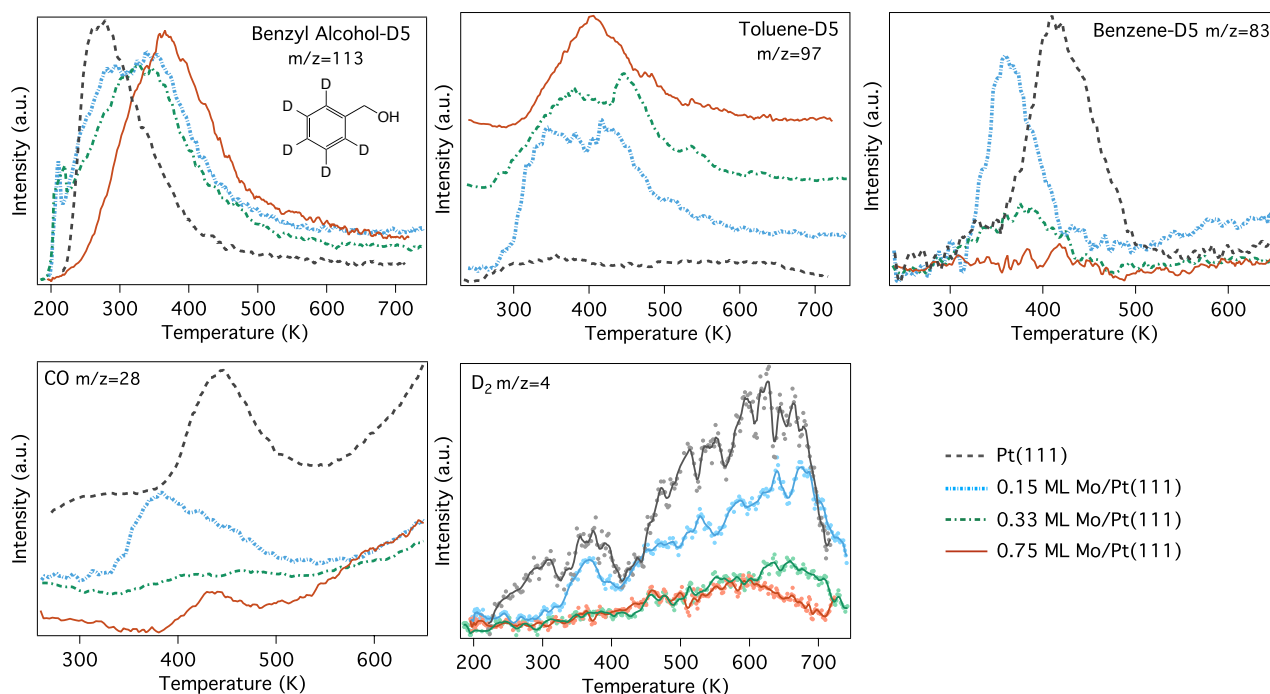


Figure 3.2: TPD spectra of benzyl alcohol- d_5 ($m/z=113$), toluene- d_5 ($m/z=97$), benzene- d_5 ($m/z=83$), CO ($m/z=28$), and D_2 ($m/z=4$) following an approximately saturating exposure of benzyl alcohol- d_5 at 200 K on clean and Mo-modified Pt(111) surfaces. Due to the noise in the D_2 spectra resulting from difficulty detecting low molecular weight fragments, individual data points were plotted (faint dots) and a moving average of these data (taken over three data points) was plotted over them (solid line).

An unmodified Pt(111) single crystal produced a significant amount of CO (observed in a desorption-limited peak near 445 K) and benzene (detected as a peak at 415 K), indicating that the primary reaction pathway for benzyl alcohol is decarbonylation. This process presumably occurs via initial dehydrogenation to benzaldehyde, which is known to undergo extensive decarbonylation on Pt(111) [152]. D_2 was also produced in broad, poorly resolved peaks, indicating multiple dehydrogenation steps occurring across a wide temperature range.

When Mo was added to the catalyst (Fig. 3.2), broad desorption features for toluene were observed, indicating that addition of Mo promoted the deoxygenation reaction. The desorption yield of toluene was found to be similar across a broad range of Mo coverages, however. On the other hand, benzene, CO, and D₂ production decreased with increasing Mo coverage, consistent with a decreased extent of decarbonylation and decomposition. In addition to decreasing the yield of benzene, Mo addition also lowered its desorption temperature by approximately 50 K. This suggests that the binding energy of any benzene produced on the PtMo surfaces decreased as the coverage of Mo increased. The decreasing desorption temperature for CO with increasing Mo exposure is expected and has been reported previously for PtMo surfaces [148]. Higher Mo coverages were also observed to result in increases in the peak desorption temperature of unreacted benzyl alcohol.

To more easily discriminate between water produced from deoxygenation reactions and water from the background, TPD experiments were performed on Pt(111) and 0.12 ML Mo/Pt(111) by pre-covering the surface with D and then adsorbing a saturating coverage of benzyl alcohol-d₅. The resulting spectra can be seen in Fig. 3.3. The desorption of D₂O from the bimetallic surface over a broad range of temperatures while toluene is being produced indicates that O produced from deoxygenation was removed as water. Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) results also suggest that aromatic oxygenates do not leave O behind after deoxygenation to oxidize the surface. As shown in Fig. 3.4, deconvolutions of the Mo 3d peaks before, during, and after exposure to 13 Pa m-cresol result in the same distribution of oxidation states.

Fig. 3.5 compares the trends in TPD product yield (determined from integrated peak areas) as a function of Mo coverage. Toluene yield was observed to go through a maximum at intermediate Mo coverages, but as noted above the yield was not highly sensitive to Mo coverage between 0.1 and 0.75 ML. On the other hand, the yield of the decarbonylation products CO and benzene dropped precipitously above 0.15 ML Mo coverage. This suggests that intermediate Mo coverages can be effective in achieving higher deoxygenation activity and selectivity.

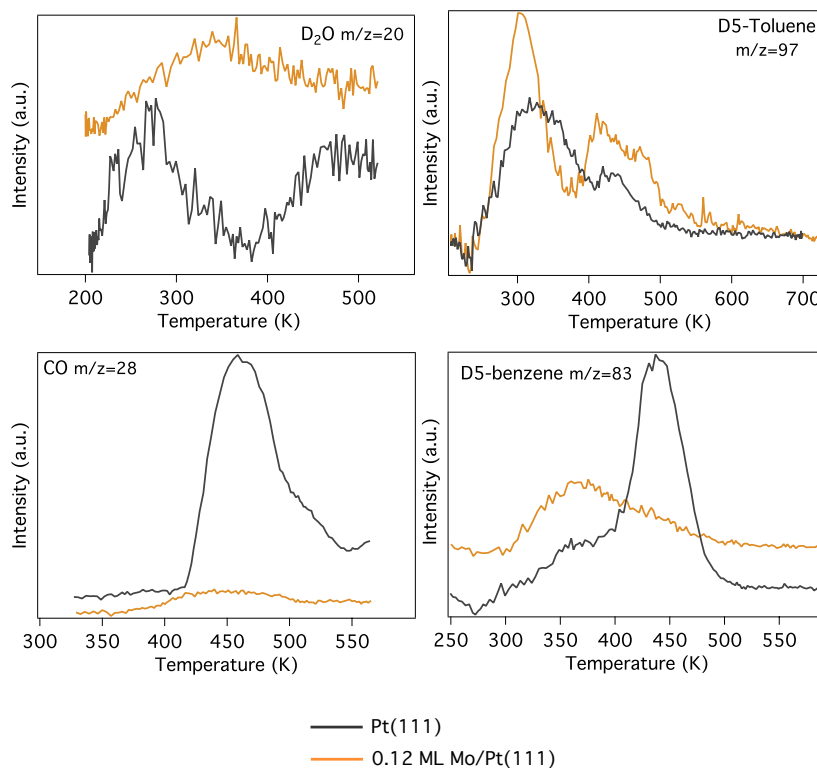


Figure 3.3: TPD spectra of D₂O ($m/z=20$), toluene-d₅ ($m/z=97$), CO ($m/z=28$), and benzene-d₅ ($m/z=83$) following an approximately saturating exposure of benzyl alcohol-d₅ at 200 K on Pt(111) and 0.12 ML Mo/Pt(111) surface that had been pre-covered with 3L D₂.

3.3.3 Toluene TPD

The changes in the benzene desorption temperature in Fig. 3.2 indicated that one effect of Mo addition to Pt(111) was to weaken aromatic binding to the surface. To further explore aromatic binding to Pt and PtMo surfaces, toluene TPD experiments were performed. Previous studies have shown that toluene may desorb unreacted or may fully decompose to form hydrogen and carbonaceous species that remain on the surface [153]. In addition, a trace amount of benzene was produced on the unmodified Pt(111) surface. Toluene and hydrogen spectra resulting from similar initial coverages of toluene can be seen in Fig. 3.6.

Similar to the results of benzyl alcohol decomposition, the hydrogen desorption spectra indicate that on a clean Pt surface toluene underwent significant decomposition, while on the

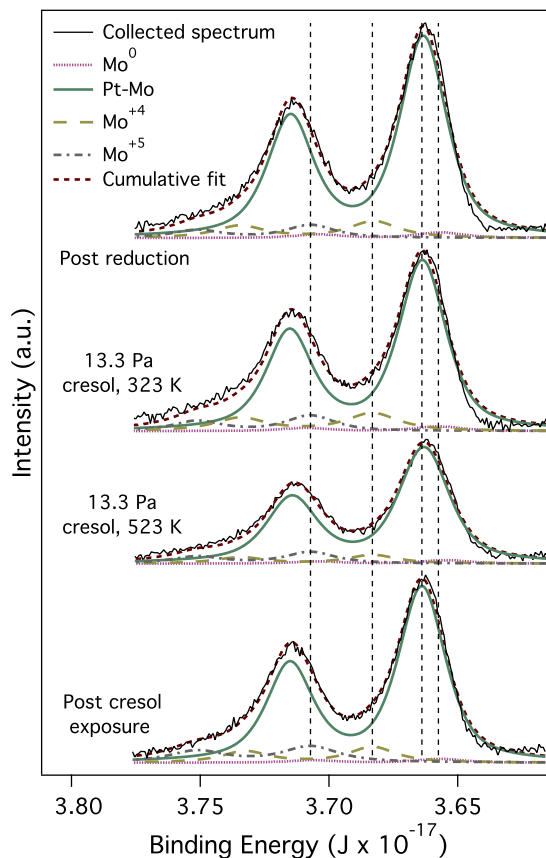


Figure 3.4: Ambient-pressure X-ray photoelectron spectra of Mo 3d peaks taken on approximately 0.3 ML Mo on Pt(111) after: reduction, exposure to 13 Pa m-cresol at 323 and 523 K, and in vacuum after exposure to m-cresol for approximately 2 h. Details of the experimental set up and peak deconvolutions can be found in a previous report [148].

Mo-modified surfaces it did not. Although a small H_2 desorption yield was measured for a surface covered with 0.15 ML Mo, negligible yield was obtained beyond that coverage. These peaks were integrated to estimate the hydrogen yield from toluene decomposition by comparing this value to the peak area on a saturated surface. For the unmodified Pt(111) surface the hydrogen spectra corresponds to 1.8 ML of hydrogen. This drops to 0.29 ML on the 0.15 ML Mo-coated surface. It should be noted that the hydrogen desorption peak does not capture all of the toluene decomposition occurring because some C_xH_y surface fragments may persist to high temperatures. Interestingly, the toluene desorption peak on Mo-covered surfaces was also significantly narrower than on the unmodified Pt(111) surface. This suggests than on the bimetallic surfaces the majority of the

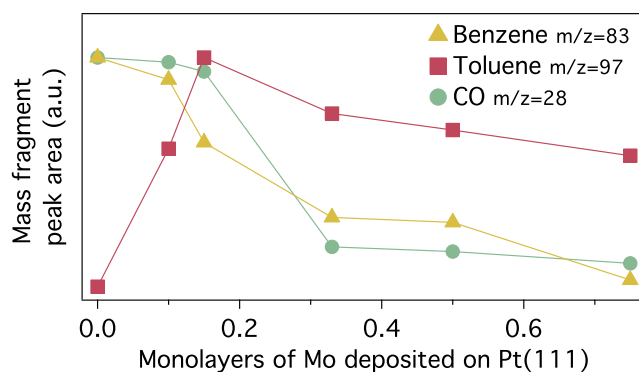


Figure 3.5: Integrated peak areas from the hydrogenolysis pathway (toluene, plotted in red squares) and the decarbonylation pathway (benzene, plotted in yellow triangles; CO plotted in green circles) shown as a function of Mo coverage. On unmodified Pt(111) (0 ML Mo) there is high selectivity to CO and no toluene production; with increasing Mo coverage the selectivity to hydrogenolysis increases and decarbonylation decreases.

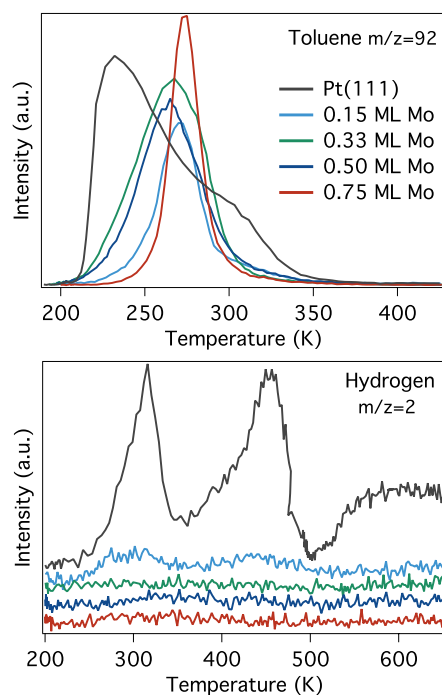


Figure 3.6: TPD spectra of toluene ($m/z=92$) and hydrogen ($m/z=2$) from a consistent exposure of toluene at 200 K on clean and Mo-modified Pt(111) surfaces.

toluene is adsorbed in the same conformation. The broad shape of the toluene peak desorbing from Pt(111) indicates there are multiple adsorbed states; this was observed in previous reports

as well [153]. The TPD results reported here show that of the toluene adsorption states that are bound weakly enough to desorb intact from Pt(111), a significant fraction of these desorb at higher temperatures than on the bimetallic surfaces.

3.3.4 Methoxyethanol TPD

The above results indicate that Mo incorporation on Pt(111) strongly affects the surface chemistry of aromatic reactants, one of which also contains alcohol functionality. A key question is whether Mo addition can also have a strong influence on reaction pathways of oxygenates that do not contain an aromatic functionality. To examine this, the aliphatic compound 2-methoxyethanol was used in TPD experiments. This probe molecule was chosen because it contains the functional groups bound to the aromatic ring in guaiacol, a frequently studied model compound to represent the lignin-derived portion of pyrolysis oil [154]. One investigation of guaiacol hydrodeoxygenation (HDO) over noble metal and bimetallic catalysts saw that over Pd/C the major product formed was phenol, resulting from cleaving the ether bond and leaving the alcohol in tact [65]. However, a bimetallic PdFe/C catalyst showed increased activity for complete deoxygenation, removing both the ether and the alcohol functional groups [65]. Therefore, it may be informative to investigate whether selectivity to reaction at the ether or alcohol functional group is influenced by modifier sites in the absence of the aromatic ring as well.

Estimations of bond dissociation energies showed that for aliphatic compounds the ether C-O bond is 46 kJ/mol weaker than an alcohol C-OH bond [38]. For 2-methoxyethanol this weaker ether bond was found to break similarly, regardless of whether or not the surface had been modified, shown in Fig. 3.7. For similar exposures of 2-methoxyethanol comparable yields of acetaldehyde, hydrogen, and CO were produced from cleavage of the ether C-O bond. A previous TPD and DFT investigation of ethanol on Pt(111) found minimal C-O scission, attributed to the higher barrier compared to C-C scission [87]. While tuning the d-band center was found to improve reforming activity to form syngas, C-O scission was still minimal [87]. Similarly, the spectra in Fig. 3.7 show that incorporation of a Mo modifier that influenced the surface chemistry of benzyl alcohol and

toluene did not change the product distribution of 2-methoxyethanol. As in the example of ethanol, this may indicate that even altering the electronic properties of the catalyst may not be sufficient to change the type of bond that is broken in this simple oxygenate. This suggests that while oxophilic metal addition may aid in targeting C-O scission in some cases, reactants that preferentially break a weak C-O bond on monometallic surfaces may not be greatly influenced.

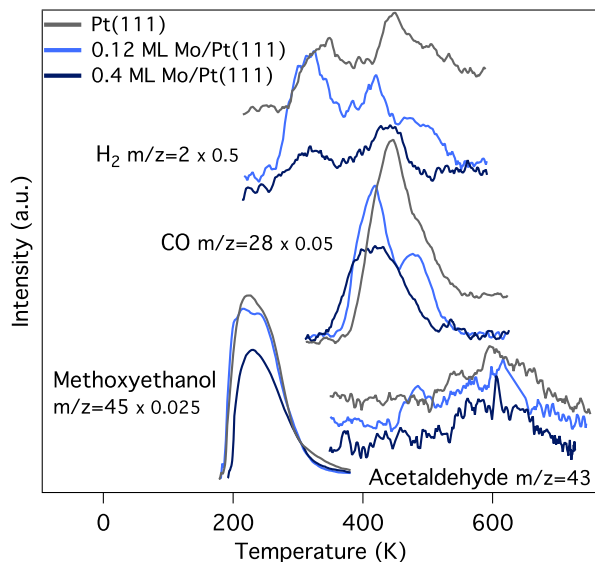


Figure 3.7: TPD spectra of hydrogen ($m/z=2$), CO ($m/z=28$), acetaldehyde ($m/z=43$) and unreacted 2-methoxyethanol ($m/z=45$) following an approximately saturating exposure of 2-methoxyethanol at 200 K on clean and Mo-modified Pt(111) surfaces.

3.3.5 DFT calculations

DFT calculations were performed to better understand the cause of the trends observed for aromatic adsorbates. Various Mo cluster sizes were tested by substituting Mo atoms into the Pt(111) lattice (Fig. 3.1). Mo clusters of 1, 3, and 4 atoms, as well as an entire monolayer of Mo, were substituted into the Pt(111) slab. Toluene was chosen as an adsorbate to probe the interaction of aromatics with these bimetallic surfaces in the absence of potential contributions from oxygen containing functional groups. The calculated adsorption energies are reported in Table 3.1 and visualizations of the optimized configurations for Pt(111) and single Mo atoms in the second and

third surface layers can be seen in Fig. 3.8.

Table 3.1: Difference in toluene adsorption energy between bimetallic PtMo surfaces of varying Mo cluster sizes and locations within the slab and an unmodified Pt(111) surface. Positive values indicate weaker binding to the surface for this exothermic process. Adsorption energy on the Pt(111) surface was calculated to be -4.12×10^{-19} J.

Surface layer containing Mo cluster	Decrease in toluene adsorption energy relative to Pt(111) ($\text{J} \times 10^{-19}$)			
	1 Mo atom	3 Mo atoms	4 Mo atoms	Monolayer
First	-0.14	-0.87	-1.65	-1.79
Second	1.47	1.46	1.46	1.44
Third	.064	0.61	1.04	1.38

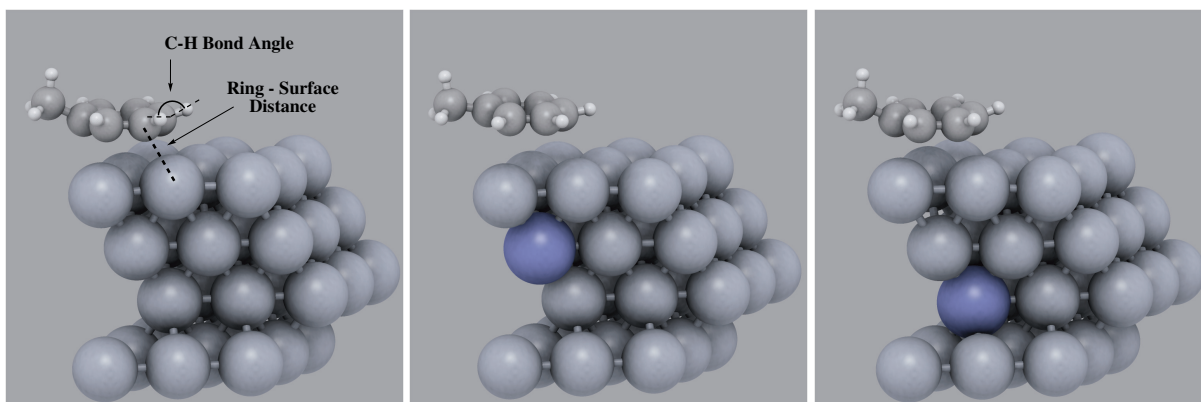


Figure 3.8: Minimum calculated energy configuration of toluene adsorbed on a Pt or PtMo surface. Mo clusters ranging from a single atom to an entire monolayer were substituted into various surface layers of a Pt(111) slab.

As seen in Table 3.1, when Mo sites are incorporated into the surface layer a toluene adsorbate interacts with them more strongly than with an unmodified Pt(111) surface. However, previous computational [9, 111] and experimental [126, 148] studies have suggested that reduced Mo prefers to migrate into the Pt subsurface.

Incorporation of Mo into the second layer reduced the toluene binding energy by 1.5×10^{-19} J, regardless of the Mo cluster size. As the Mo sites were placed further into the subsurface, the toluene binding strength and adsorption configuration (shown for Mo in the third layer in Fig. 3.8) began to approach those values seen for adsorption on unmodified Pt(111). In the case of a single

Mo atom, this transition was rapid when the modifier was placed in the third layer, with toluene adsorption being nearly identical to that on unmodified Pt(111). The trend was more gradual as cluster size increased. This trend is expected, as early transition metals in the subsurface tend to lower the d-band center of the surface Pt atoms [17]. If the modifier sites are too far into the subsurface to interact with the surface Pt, this d-band shift will not be significant.

The distance between the aromatic ring and the surface, measured as the distance from a ring carbon atom to a Pt site directly underneath it on each surface and the C-H bond angle (see Fig. 3.8) are reported in Table 3.2. While all bond angles were nearly identical, for consistency the reported angle is shown for the hydrogen bound to the ring carbon alpha to the methyl group. These values further demonstrate the ring repulsion and rehybridization. The strong interaction between toluene and Pt(111) has previously been shown to affect the molecular structure, resulting in changing C-H bond angles on the aromatic ring [155, 156].

Table 3.2: Distance between aromatic ring and the surface (x) and the C-H bond angle (θ) for Pt and PtMo surfaces (as labeled in Fig. 3.8)

	Pt(111)		1 Mo atom		3 Mo atoms		4 Mo atoms		Monolayer	
Surface layer containing Mo cluster	x (nm)	θ ($^{\circ}$)	x (nm)	θ ($^{\circ}$)	x (nm)	θ ($^{\circ}$)	x (nm)	θ ($^{\circ}$)	x (nm)	θ ($^{\circ}$)
Second (or n/a for Pt(111))	0.22	160.7	0.29	179.2	0.30	177.5	0.39	179.3	0.31	179
Third			0.22	161.9	0.23	165.2	0.27	171.2	0.27	179.4

DFT calculations were also performed to support the hypothesis that a large fraction of the Mo migrates subsurface on Mo/Pt(111). While this has been shown for a bare surface using XPS in a previous investigation [148] it is possible that introducing an oxygenate such as benzyl alcohol may pull the Mo to the surface. To test this, the adsorption energy of OH on various PtMo surfaces was calculated. As shown in Table 3.3, the adsorption energy of OH increases dramatically when it is bound to a surface Mo site. However, when Mo is subsurface the OH adsorption energy is nearly the same as on unmodified Pt(111). Similarly, H adsorption energies were calculated on the

same surfaces and also were bound more strongly when Mo was incorporated into the surface layer (Table 3.4).

Table 3.3: OH adsorption energies ($\text{J} \times 10^{19}$) on Pt and PtMo surfaces. Larger negative values indicate stronger binding.

Surface layer containing Mo cluster	OH adsorption energy on each surface ($\text{J} \times 10^{-19}$)			
	Pt(111)	1 Mo atom	3 Mo atoms	Mo ML (9 Mo atoms)
First (or n/a for Pt(111))	-4.33	-6.41	-6.57	-7.69
Second		-4.33	-4.17	-4.17
Third		-4.17	-4.17	-3.52

Table 3.4: H adsorption energies ($\text{J} \times 10^{19}$) on Pt and PtMo surfaces. Larger negative values indicate stronger binding.

Surface layer containing Mo cluster	H adsorption energy on each surface ($\text{J} \times 10^{-19}$)			
	Pt(111)	1 Mo atom	3 Mo atoms	Mo ML (9 Mo atoms)
First (or n/a for Pt(111))	-4.65	-4.49	-4.65	-5.45
Second		-4.49	-4.01	-3.52
Third		-4.49	-4.49	-4.49

Using the hypothesis that at least a large population of the Mo atoms are located subsurface, DFT calculations were performed to probe the adsorption energy and orientation of benzyl alcohol on Mo/Pt(111) with subsurface Mo atoms using the analogous alkoxide. The adsorbate was placed on the surface in the same flat lying conformation over Pt(111) as well as two bimetallic surfaces with 1 and 3 Mo atoms in the second layer; the resulting systems were then relaxed. The final optimized orientations can be seen in Fig. 3.9. Similar to the results using toluene, these images show that incorporation of Mo alters the adsorption orientation by repelling the aromatic ring. For comparison of the three surfaces, the distance from the surface to the carbon atom of the ring which the pendant group is bound to can be seen in Table 3.5. Additionally, incorporation of Mo reduced the adsorption strength of the alkoxide; the relative adsorption energies referenced to binding on Pt(111) can also be seen in Table 3.5.

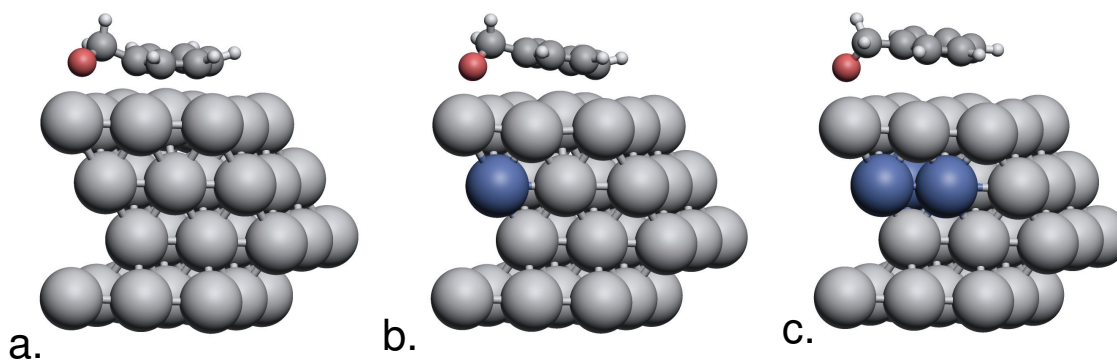


Figure 3.9: Images of relaxed surfaces of benzyl alkoxide on a. Pt(111), b. 1 Mo atom in Pt(111), and c. 3 Mo atoms in Pt(111).

Table 3.5: Summary of DFT calculations of benzyl alkoxide on Pt(111) and Mo/Pt(111). The distance from the surface to the carbon atom of the ring which the pendant group is bound to is reported (labeled carbon-surface bond distance), along with the relative adsorption energy on each surface shown in Fig. 3.9, referenced to binding on Pt(111) (Fig. 3.9a.). A positive difference in adsorption energy indicates weaker binding to the bimetallic surface.

Surface	Carbon-surface bond distance (nm)	Adsorption energy difference relative to Pt(111) ($\text{J} \times 10^{-20}$)
Pt(111)	0.22	
1 Mo atom (Fig. 3.9b.)	0.28	8.97
3 Mo atoms (Fig. 3.9c.)	0.32	9.77

3.3.6 Reactor studies

A key question is how the observations from surface science studies relate to experiments conducted on non-model materials, namely supported Pt and PtMo nanoparticles. To explore how Mo incorporation affects hydrogenation reactions of aromatic reactants, differential rate measurements were carried out on alumina-supported Pt and PtMo catalysts. Experiments were also carried out at higher conversions but the selectivity to hydrogenolysis vs decarbonylation was not significantly impacted; the main change as conversion increased was the production of additional benzene from the benzaldehyde intermediate. The TPD experiments reported above represent the activity on a dynamic surface; as products are formed and desorb the crowding

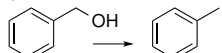
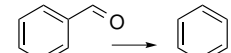
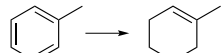
of the surface is significantly impacted. This is also a batch system. To translate this to the activity on hydrogen-covered nanoparticles in a flow reactor, low conversion may be desirable to probe the reaction pathways in a less complex environment, without potential contributions from high coverage of intermediates. Furthermore, by performing differential rate measurements, investigations of apparent activation energies may be performed to further investigate potential changes in reaction mechanism upon Mo incorporation.

Pt and PtMo catalysts prepared via co-impregnation on an alumina support were investigated for benzyl alcohol HDO. These catalysts have been characterized previously [9] and were found to have small metal particles (about 1-2 nm). These catalysts will be discussed in more detail in the following chapter. To investigate the reaction mechanism a series of initial rate experiments were conducted using benzyl alcohol to study HDO as well as the intermediate product benzaldehyde, which is the precursor to decarbonylation products benzene and CO. These results can be seen in Table 3.6. In contrast to the UHV results, there was no dramatic change in decarbonylation or hydrogenolysis rates upon addition of Mo. As shown in Table 3.6, using benzaldehyde as the reactant, rates of benzene production were the same over all catalysts (within error). At constant partial pressures and varying temperatures between 353 - 413 K the apparent activation energies increased slightly with Mo incorporation, 8.7, 17, 23 kJ/mol over Pt/Al₂O₃, Pt₁₀Mo₁/Al₂O₃, and Pt₁Mo₁/Al₂O₃ respectively. However, this did not result in a notable change in selectivity or activity for either pathway. The hydrogenolysis pathway, to produce the desired product toluene, was also investigated by measuring the rate of toluene production from feeding benzyl alcohol over Pt/Al₂O₃, Pt₁₀Mo₁/Al₂O₃, and Pt₁Mo₁/Al₂O₃ (Table 3.6). There was a slight increase in rate with incorporation of Mo, but not dramatic and certainly not as notable as the increase in toluene production seen in UHV for PtMo surfaces. The apparent activation energy for hydrogenolysis of benzyl alcohol to toluene over these catalysts was calculated to be 40, 40, 41 kJ/mol respectively. These values are not statistically different, indicating there was no change in apparent activation energy for hydrogenolysis with Mo incorporation.

Interestingly, one difference that was observed over the incipient wetness prepared PtMo

catlysts was in the hydrogenation of toluene to methylcyclohexene (Table 3.6). It was observed that a Pt_1Mo_1 catalyst exhibited approximately half the turnover frequency for this ring hydrogenation reaction compared to an unmodified catalyst, consistent with a weaker aromatic-surface interaction. This effect was not as apparent for a more dilute $\text{Pt}_{10}\text{Mo}_1$ catalyst.

Table 3.6: Differential rates of product formation from reacting benzyl alcohol, benzaldehyde, or toluene over Pt and PtMo alumina-supported catalysts at 413 K, 1 atm. Rates were measured at the same partial pressure of the reactant over each catalyst. This result appears to contrast with the lower decarbonylation yield measured during benzyl alcohol TPD on Pt(111).

	Initial rates ($\mu\text{mol}/\text{m}^2$ catalyst) at 353 K (benzyl alcohol HDO and benzaldehyde decarbonylation) or 413 K (toluene hydrogenation)		
	Benzyl alcohol HDO (<5% conversion) 	Benzaldehyde decarbonylation (<5% conversion) 	Toluene hydrogenation (<10% conversion) 
$\text{Pt}/\text{Al}_2\text{O}_3$	7 ± 1	34 ± 4	879 ± 27
$\text{Pt}_{10}\text{Mo}_1/\text{Al}_2\text{O}_3$	12 ± 2	35 ± 9	808 ± 13
$\text{Pt}_1\text{Mo}_1/\text{Al}_2\text{O}_3$	12 ± 2	35 ± 9	$460. \pm 4$

HDO is expected to be sensitive to particle size; benzyl alcohol HDO was also investigated on catalysts with larger average particle sizes. A commercial 5 wt% $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst was used as a control case and to investigate the effect of Mo on this catalyst, 1.5 wt% Mo was deposited on it through incipient wetness impregnation. The rates of product formation on both the Pt and PtMo catalysts are reported in Fig. 3.10. Similarly to the results of the UHV studies reported above, incorporation of Mo to the Pt catalyst reduced the selectivity to decarbonylation and increased toluene production. To further support the conclusion from the UHV results that this change in reaction pathway selectivity is a synergistic effect from Pt-Mo sites interacting, a monometallic Mo catalyst was also tested. It showed much lower activity than the Pt based catalysts, and did not have high rates of toluene production. Because benzene is a product formed in series from the decarbonylation of benzaldehyde, we also conducted experiments in which benzaldehyde was used as a feed at the same reaction conditions. In these experiments, we measured the rate of benzene production to be $0.24 \pm 0.01 \text{ mmol} \cdot \text{m}^2 \text{ catalyst}^{-1}$ over Pt and $0.10 \pm 0.04 \text{ mmol} \cdot \text{m}^2 \text{ catalyst}^{-1}$ over PtMo.

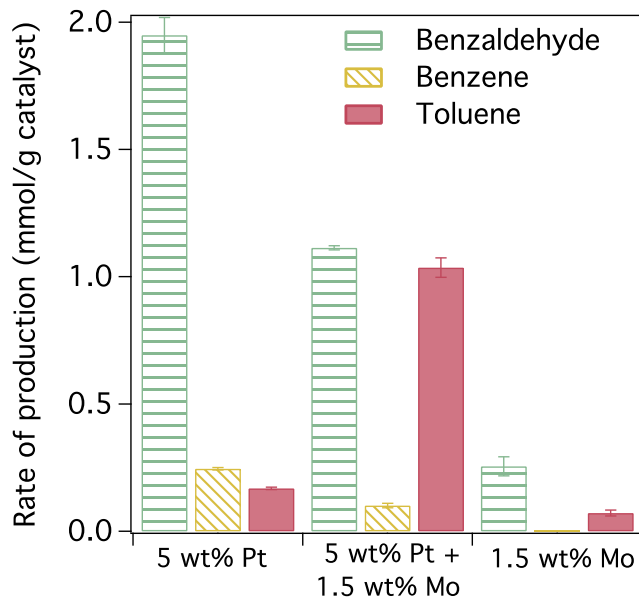


Figure 3.10: Rates of product formation from reacting benzyl alcohol over Pt and PtMo catalysts at 413 K and <3% conversion. Error bars represent a 95% confidence interval calculated based on at least 3 replicate data points.

3.3.7 Catalyst characterization

CO chemisorption was performed on the commercial 5 wt% Pt/ Al_2O_3 catalyst both as purchased and after addition of 1.5 wt% Mo. Table 3.7 shows the resulting surface areas. Deposition of Mo on top of the Pt/ Al_2O_3 catalyst increased the average particle size and decreased the active metal surface area, consistent with the characterization results of the incipient wetness prepared Pt, $\text{Pt}_{10}\text{Mo}_1$, and Pt_1Mo_1 catalysts discussed above for toluene hydrogenation [9]. TEM was also performed to analyze particle sizes.

Table 3.7: Surface area and metal dispersion measured by CO chemisorption and particle sizes measured using TEM on Pt and PtMo catalysts. Error bars represent the 95% confidence interval calculated using 3 replicate samples for surface area and dispersion and at least 100 particles for particle size.

Catalyst	Surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Dispersion (%)	Particle diameter (nm)
Pt/ Al_2O_3	3.3 ± 0.1	22.2 ± 0.8	4.2 ± 0.2
PtMo/ Al_2O_3	2.6 ± 0.1	13.7 ± 0.1	5.4 ± 0.2

3.4 Discussion

Previous UHV studies of benzyl alcohol on Pd(111) have shown that the reaction can take two pathways depending on the orientation with which it adsorbs on the surface [75]. These can be seen in Fig. 3.11.

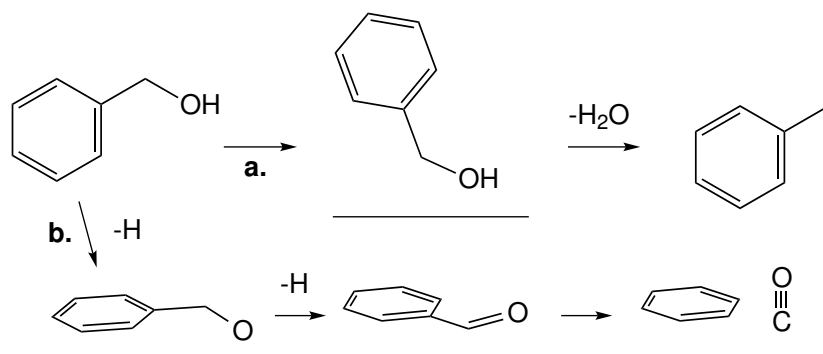


Figure 3.11: Reaction pathways for benzyl alcohol on noble metal surfaces: a. upright adsorption leading to hydrogenolysis and b. flat-lying adsorption leading to decarbonylation. Adapted from [75].

The previous study indicated that when benzyl alcohol adsorbs in an upright orientation (Fig. 3.11a) with the ring perpendicular to the surface, C-O bond scission (hydrogenolysis) is favored to produce toluene. In contrast, if it adopts a flat lying structure, as shown in Fig. 3.11b, with the ring parallel to the surface, it undergoes decomposition to hydrogen and decarbonylation to form benzene and CO [75]. Similar trends were observed for the aromatic reactant furfuryl alcohol [74]. For the approximately saturating exposure of benzyl alcohol shown in Fig. 3.2, toluene was not produced in an appreciable amount on Pt(111). Instead, decarbonylation was favored, producing benzene and CO. Evidence of ring decomposition, produced from intermediates very strongly bound to the surface, was also observed through desorption of D_2 . One commonly suggested method to disfavor strong adsorption through the aromatic function is via surface crowding [157]. For instance, coadsorbed hydrogen has previously been shown to decrease the adsorption strength of ethylene [158]. Interestingly, toluene was produced during benzyl alcohol TPD on a D-precovered Pt(111) surface (Fig. 3.3), whereas no toluene was detected from clean Pt(111). While decarbonylation was

still dominant, shown by the large benzene and CO peaks, the presence of preadsorbed D on the surface promoted the deoxygenation pathway. This may suggest that coadsorbed D may help crowd the surface to favor formation of some upright structures similar to those shown in Fig. 3.11a. The availability of additional deuterium to participate in the dehydration to toluene may also play a role, however.

In contrast to results on Pt(111), on Mo/Pt(111) toluene production was observed and the formation of decarbonylation products decreased. Previous studies of aromatic oxygenates have found that incorporation of oxophilic metals can improve selectivity to C-O scission, which has been proposed to be due to orientation effects [32, 152, 159, 160]. For example, the aldehyde analog to benzyl alcohol, benzaldehyde, was studied on Pt(111) and Zn/Pt(111). Benzaldehyde was shown through high-resolution electron energy loss spectroscopy (HREELS) to adsorb in a flat-lying conformation on unmodified Pt, strongly interacting with the surface and resulting in decomposition to CO, H₂, and small hydrocarbon fragments [152]. Alternatively, on a Zn-decorated surface, benzaldehyde adsorbed through its carbonyl group onto a Zn site, with the aromatic ring repelled from the surface, resulting in C-O bond scission to produce toluene [152].

Previous studies have shown that a variety of aromatic compounds prefer to adsorb on metals such as Rh, Pt, Ni, and Pd in flat-lying configurations at low coverage [161–165]. This flat lying geometry results in poor selectivity to deoxygenation reactions. For instance, furfural primarily undergoes decarbonylation on Ni/SiO₂ [159]. However, when Fe was added as an oxophilic promoter, the bimetallic NiFe/SiO₂ showed increased hydrogenolysis selectivity, which was attributed to an alteration of preferred adsorption orientation by the increased metal-oxygen bond strength [159]. The same trend was observed with m-cresol as the reactant. Ni catalysts were found to interact preferentially with the aromatic ring, resulting in ring hydrogenation products; on NiFe catalysts the preferred adsorption was through the oxygen atom, resulting in deoxygenation to form toluene [32]. Furthermore, computational studies showed that Fe actually repelled the π electron system of the ring; NiFe surfaces with large enough Fe domains could be especially active for hydrogenating the carbonyl group without ring hydrogenation [32].

These examples illustrate the potential for an oxophilic modifier to alter the adsorption of the reactant by decreasing the interaction between aromatics and the surface. We hypothesize that the relatively decreased extent of aromatic-surface interaction may be due to at least one of two effects: (1) oxophilic modifier sites that strongly interact with oxygen containing functional groups can perturb the adsorption geometry of aromatic oxygenates by effectively “pulling” the oxygen atom closer to the surface, as found for m-cresol adsorption on a Mo-modified Pt(111) surface in computational studies [9]; or, (2) the modifier may also have a ligand effect and modify the electronic structure of the other metal [17, 127, 166, 167]. A common explanation for the observed difference in preferred adsorption orientation in many of these systems is a d-band shifting effect. By alloying two metals to lower the d-band center the antibonding orbitals are shifted to lower energy and are therefore more highly populated than in a monometallic sample; this decreases how strongly adsorbates bind to the bimetallic surface [168].

Understanding the state of the PtMo surface is important in better understanding the mechanisms by which this bimetallic system results in improved deoxygenation selectivity. The modifier sites may be present in the surface or subsurface layers. Previous experimental and computational studies have suggested that on Pt(111), Mo prefers to migrate to the subsurface when reduced [111, 126, 127, 148]. The experimental results reported here are also consistent with this hypothesis. DFT calculations for OH adsorption on Pt and PtMo surfaces showed that while OH binds more strongly when Mo is in the surface layer, this is not the case for subsurface Mo (Table 3.3). Our previous results showed that hydrogen desorption temperatures decrease as Mo coverage increases [148]. However, DFT calculations show H is adsorbed more strongly on a PtMo surface where Mo is located in the surface layer (Table 3.4), supporting the hypothesis that the modifier sites are located subsurface.

Our previous AP-XPS results showed attenuation of the Mo 3d signal and an increase in the Pt 4f signal intensity between deposition and annealing at 800 K [148]. The inelastic mean free path of electrons through the sample at the energy of the incident X-ray beam was about 0.79 nm [169]. At an estimated 0.23 nm between layers in a Pt(111) surface [170], this means that the

signal would be attenuated by about 26% in the second layer, 46% in the third layer, and 60% in the third layer [171]. Considering that the observed signal attenuation was about 15%, it is reasonable to assume that the majority of the Mo is in the subsurface, given that some of the Mo may be in the subsurface even before annealing. Furthermore, the AP-XPS results suggest that aromatic oxygenates do not oxidize a PtMo surface. A 0.3 ML Mo/Pt(111) surface was exposed to 13 Pa of *m*-cresol at 323 and 523 K; the peak positions did not shift and deconvolutions showed no significant change in oxidized Mo species (Fig. 3.4). Collectively, this evidence suggests that the majority of Mo sites remained in the subsurface, altering the electronic structure of the Pt surface atoms and the adsorption strength of reactants.

The results from toluene TPD (Fig. 3.6) and DFT calculations (Table 3.1) are also consistent with the presence of subsurface Mo that decreases the aromatic binding energy. Direct comparisons between experimental and DFT results are complicated by the presence of coadsorbates (including neighboring aromatics) during the experiments. The presence of coadsorbates during TPD would be expected to destabilize toluene adsorption compared to the low-coverage conditions of the DFT calculations [78, 172–174].

Previous studies reported that only about 5% of the toluene exposed to the Pt(111) surface desorbs intact, with the rest decomposing to produce large quantities of H_2 [153]. However, we found that incorporation of Mo dramatically decreased the production of hydrogen. As noted above, the high-temperature shoulder in the toluene desorption spectra in Fig. 3.6 is also consistent with a more strongly-bound state of toluene. The DFT calculations supported this explanation as well; both the calculated adsorption energies in Table 3.1 and the visualizations of the lowest energy orientation in Fig. 3.8 suggest that incorporation of Mo in the subsurface repels the aromatic ring from the surface and prevents loss of aromaticity. The DFT results reported in Table 3.1 also are consistent with shifts in desorption temperature seen experimentally in Fig. 3.6. Thus, the weaker aromatic-surface interactions observed during TPD on PtMo surfaces are consistent with DFT models that incorporate Mo in the subsurface.

Benzyl alcohol hydrodeoxygenation (HDO) was extended to supported catalysts as well. The

decreased hydrogenation rate of toluene over incipient wetness prepared PtMo, even with similar rates of hydrogenolysis and decarbonylation, may be due to the weaker binding of toluene to the bimetallic surface, as shown in the TPD and DFT studies. These catalysts are well mixed and have Pt-Mo sites that are interacting; detailed characterization of these materials will be discussed in the following chapter. On the Pt catalyst the toluene produced from benzyl alcohol hydrogenolysis may be bound strongly enough that it remains on the surface a sufficient length of time to begin hydrogenation. Benzene hydrogenation was previously shown to be structure insensitive on platinum catalysts; the turnover frequency did not depend on particle size (varied between 1-5 nm) or Pt precursor used [175]. Since the Pt site distribution is likely not responsible for this decreased hydrogenation activity over PtMo surfaces, we hypothesize that it is due to decreased adsorption strength due to Mo incorporation. Similar trends were observed in a previous study of benzene hydrogenation on noble metal catalysts. On Ru/SiO₂ partial hydrogenation of benzene was observed; this was suppressed with incorporation of Zn [176]. It was proposed that this could be due to weaker benzene adsorption on the Ru-Zn surface [176].

Decreased toluene hydrogenation compared to decarbonylation or deoxygenation may be due to a particle size effect. HDO rates are expected to be particularly sensitive to particle size. Undercoordinated sites are more reactive than terrace sites and have been previously shown to catalyze deoxygenation of aromatic oxygenates [177]. Controlling the availability of these undercoordinated sites has previously been shown to influence selectivity to furfural HDO over decarbonylation by coating the surface with alkanethiolates so that availability to terrace sites was severely decreased [77]. The catalysts used for the data displayed in Table 3.6 had small particle sizes, about 1-2 nm [9]. Because these small particles contain a large fraction of defect sites [178] benzyl alcohol HDO was also studied over larger particles of Pt and PtMo. Unlike on the small particles of the incipient wetness prepared catalysts, incorporation of Mo did increase the rate of HDO. The initial rate data shown in Fig. 3.10 were measured at low conversion (<3%); because the decarbonylation pathway is a series reaction in which benzaldehyde is formed as an intermediate (Fig. 3.11b), the rate of benzene production is low on both catalysts. However, when

the dehydrogenation rate is considered by adding the rates of benzene and benzaldehyde production, this pathway decreases from $0.66 \text{ mmol} \cdot \text{m}^2 \text{ catalyst}^{-1}$ on Pt to $0.47 \text{ mmol} \cdot \text{m}^2 \text{ catalyst}^{-1}$ on PtMo. Meanwhile the hydrogenolysis rate (Fig. 3.11a) increases from 0.06 to $0.4 \text{ mmol} \cdot \text{m}^2 \text{ catalyst}^{-1}$

These results are consistent with the UHV results for Pt and PtMo surfaces, however the effect of Mo incorporation is less dramatic. Whereas the Mo/Pt(111) surfaces drastically suppressed decarbonylation with only 0.33 ML Mo, a 1.5 wt% Mo, 5 wt% Pt catalyst still showed appreciable activity for decarbonylation (Fig. 3.10). Similarly, Pt(111) produced no toluene while Pt/Al₂O₃ did. It is likely that this difference is due to the surface structure of the two systems. While the UHV studies were performed on Pt(111), there are a significant number of defect sites on the supported catalysts that may alter reactivity. While the commercial Pt catalyst contained larger particle sizes than the incipient wetness prepared sample, there is still some population of defect sites (5 nm particles contain about 70% terrace sites [178]). On Pt/Al₂O₃ the presence of these defect sites may provide sites for hydrogenolysis even in the absence of Mo. However, since these particles still contain a large fraction of (111) facets, these supported catalysts still largely follow the trends from the UHV studies.

3.5 Conclusions

Benzyl alcohol was shown to undergo decarbonylation to form benzene and CO as well as complete decomposition to produce hydrogen and carbonaceous surface species over Pt(111). Incorporation of Mo onto the surface suppressed these pathways and introduced a hydrogenolysis pathway to produce toluene. DFT calculations suggest that this may be due to Mo addition causing the aromatic ring to be repelled from the surface, altering the adsorption orientation as well as reducing the adsorption strength. This was also supported by toluene TPD experiments, which showed less decomposition after deposition of Mo on the Pt(111) surface. Vapor-phase reactor studies on supported Pt and PtMo catalysts agree with these surface science results, with increased activity for hydrogenolysis on the bimetallic catalyst.

Chapter 4

Enhanced hydrodeoxygenation of m-cresol over bimetallic Pt-Mo catalysts through an oxophilic metal-induced tautomerization pathway

Supported bimetallic catalysts consisting of a noble metal (e.g., Pt) and an oxophilic metal (e.g., Mo) have received considerable attention for the hydrodeoxygenation of oxygenated aromatic compounds produced from biomass fast pyrolysis. Here, we report that PtMo can catalyze m-cresol deoxygenation via a pathway involving an initial tautomerization step. In contrast, the dominant mechanism on monometallic Pt/Al₂O₃ was found to be sequential Pt-catalyzed ring hydrogenation followed by dehydration on the support. Bimetallic Pt₁₀Mo₁ and Pt₁Mo₁ catalysts were found to produce the completely hydrogenated and deoxygenated product, methylcyclohexane (MCH), with much higher yields than monometallic Pt catalysts with comparable metal loadings and surface areas. Over an inert carbon support, MCH formation was found to be slow over monometallic Pt catalysts while deoxygenation was significant for PtMo catalysts even in the absence of an acidic support material. Experimental studies of m-cresol deoxygenation together with density functional theory calculations indicated that Mo sites on the PtMo bimetallic surface dramatically lower the barrier for m-cresol tautomerization and subsequent deoxygenation. The accessibility of this pathway arises from the increased interaction between the oxygen of m-cresol and the Mo sites in the Pt surface. This interaction significantly alters the configuration of the precursor and transition states for tautomerization. A suite of catalyst characterization techniques including X-ray absorption spectroscopy (XAS) and temperature programmed reduction (TPR) indicate that Mo was present in a reduced state on the bimetallic surface under conditions relevant for reaction.

Overall, these results suggest that the use of bifunctional metal catalysts can result in lowered energy barriers to promote additional reaction pathways that are unfavorable on monometallic noble metal catalysts.

4.1 Introduction

Lignocellulosic biomass is a potentially useful feedstock for production of renewable fuels and chemicals. One method of biomass conversion is ex-situ catalytic fast pyrolysis (CFP) [47, 179, 180]. Fast pyrolysis breaks down the biomass at high temperatures in the absence of oxygen [2] to produce a complex mixture of hydrocarbons and oxygenates, which includes large quantities of lignin-derived oxygenated aromatic species (i.e., phenolics) [5, 181, 182]. This complex mixture can then be catalytically upgraded in the vapor or liquid phase to improve the fuel quality and stability of the resulting bio-oil through hydrogen incorporation and oxygen removal. Phenolic compounds comprise 30-40% of the lignin fraction, [183] and are difficult to deoxygenate because of their high C-O bond strength [38]. Accordingly, selective catalytic deoxygenation of the aromatic fraction of pyrolysis oil, either in the vapor or condensed phase, is an essential step in thermochemical conversion of biomass into useful fuels and other products [64, 179, 180, 184].

A variety of catalysts have been studied for aromatic deoxygenation [47, 64, 185, 186], and noble metal catalysts have received significant attention due to their relatively high activity and stability [30, 50, 64]. As shown in Fig. 4.1, several mechanisms for deoxygenation of oxygenated aromatics have been proposed including ring hydrogenation-dehydration (Fig. 4.1a) [30, 31], direct deoxygenation (Fig. 4.1b) [187], ring hydrogenation-direct C-O scission (Fig. 4.1c) [50, 65], and a tautomerization mechanism (Fig. 4.1d) [32, 49, 52].

In addition to the active phase used, the preferred pathway depends upon the reaction conditions and the catalyst support. The most cited mechanism for supported noble metal catalysts on acidic supports is ring hydrogenation on the metal followed by dehydration on the support [30, 31, 36, 52]. Deoxygenation has also been observed in some cases over noble metal catalysts using an inert carbon support, demonstrating that aryl-O bond cleavage can occur over the metal

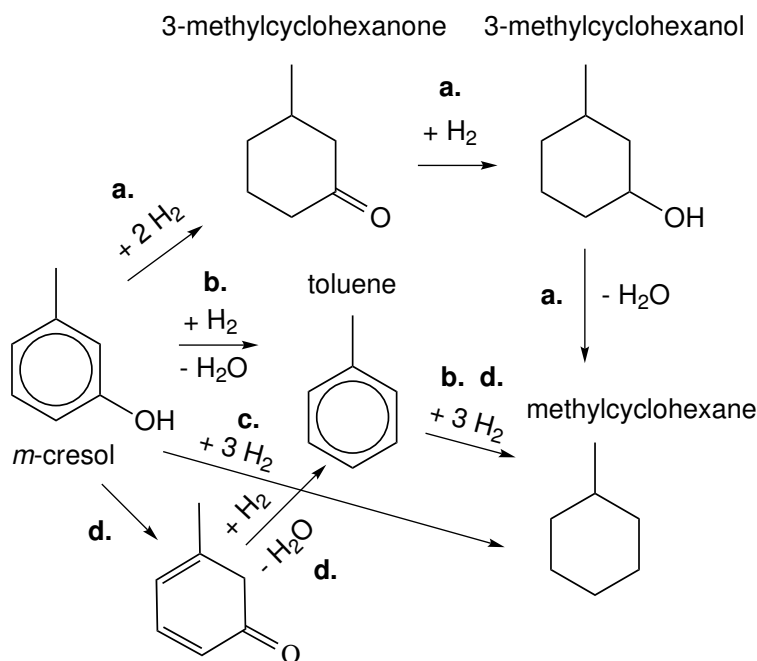


Figure 4.1: Proposed deoxygenation mechanisms over supported noble metal catalysts: a) ring hydrogenation-dehydration, b) direct deoxygenation, c) ring hydrogenation-direct C-O scission, and d) tautomerization.

active phase alone [65, 188, 189].

Bimetallic catalysts that combine oxophilic metals with noble metals exhibit promising selectivity and activity for deoxygenation reactions [35, 93, 94, 96, 97, 110, 111, 190]. For example, Rh-based catalysts that were modified with Re or Mo were shown to increase activity and selectivity in C-O bond scission reactions using cyclic ethers. One of the reactants tested, tetrahydrofurfuryl alcohol, produced 1,5-pentanediol at over 90% selectivity on the bimetallic catalysts vs. less than 60% selectivity on monometallic Rh [96]. These bimetallic catalysts have been proposed to reduce the barrier for C-O scission through a strong interaction of the oxophilic metal with the oxygen-containing moiety of the aromatic compound. This mechanism has been proposed for NiFe catalysts used for vapor-phase hydrodeoxygenation (HDO) of m-cresol to toluene [32] and for the deoxygenation of phenol by PdFe catalysts [65]. Studies on Fe-based catalysts indicate that while oxophilic metals can themselves deoxygenate m-cresol, they suffer from poisoning due to surface

oxidation [50, 52]. The addition of noble metals to these catalysts increased water desorption and the stability of the reduced Fe [50].

Previous experimental results have been complemented by computational studies [32, 50, 191]. One investigation of phenol on an Fe(110) surface showed water formation as the rate-limiting step, with a high barrier of 2.11×10^{-19} J for a stepwise mechanism of single hydrogen ring hydrogenation, C-O bond scission, and intermolecular hydrogen transfer [191]. These studies focused on isolated surface intermediates at low coverages. However, separate computational studies have suggested that the Fe(110) surface would have high hydrogen coverage at reaction temperatures and pressures [192]. Moreover, phenolic species are known to adsorb strongly to late transition metal surfaces, creating a crowded surface environment that strongly affects reaction chemistry [75]. A substantial body of previous work for other reactions, such as olefin hydrogenation, shows that high coverage of co-adsorbed surface species can strongly influence reaction mechanisms [193–195]. Furthermore, prior work has suggested that the effects of high coverage can be modeled by adsorption of a simple adsorbate such as hydrogen [158].

In this work we used a combined experimental and computational approach to elucidate the role of oxophilic metals in the deoxygenation of m-cresol, a phenolic model compound. Supported Pt catalysts with various Mo loadings were evaluated for m-cresol hydrodeoxygenation. These catalysts, as well as model PtMo surfaces, were characterized using a variety of techniques including X-ray absorption spectroscopy (XAS), chemisorption of probe molecules, and temperature-programmed reduction (TPR). XAS experiments were performed and analyzed by collaborators Singfoong Cheah and James Gallagher. Complementary density functional calculations were performed by collaborators Glen Ferguson and Gregg Beckham to map the reaction pathways for m-cresol HDO on Pt(111) with Mo atoms included in the lattice; importantly, the model included a high coverage of hydrogen to investigate the HDO chemistry on the types of crowded surfaces expected under reaction conditions. As discussed below, the combined studies strongly suggest that addition of Mo to Pt catalysts creates active sites for m-cresol tautomerization to an unstable alcohol that has a significantly lower barrier to deoxygenation.

4.2 Methods

4.2.1 Experimental methods

Catalysts were prepared by incipient wetness impregnation of a porous γ -Al₂O₃ support (Albemarle MARTOXID AN/I, 150 m²/g BET surface area, 75- μ m particle diameters). Aqueous solutions were prepared of the metal precursors using chloroplatinic acid hexahydrate (Strem Chemical Inc.) and ammonium molybdate tetrahydrate (Strem Chemical Inc.). Pt/Al₂O₃ was prepared with a nominal loading of 5 wt%. PtMo/Al₂O₃ catalysts were prepared via co-impregnation of the two precursors with a 10:1 and 1:1 atomic ratio of Pt:Mo, containing the same amount of Pt with Mo added to create the desired composition at increased total metal loading. The catalysts were dried in air at 373 K then calcined for 2 h at 723 K in 50 sccm He and 30 sccm O₂. Carbon supported catalysts were prepared using the same metal precursors and deposited on a carbon black powdered support (Vulcan XC 72R). After preparation the catalyst was dried in air at 393 K for 10 h. Elemental analysis was performed to determine actual weight loading of each metal using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

CO pulse chemisorption was performed on a Micromeritics ChemiSorb 2720 to characterize active metal surface area. Approximately 100 mg of catalyst was reduced in-situ at 673 K for 2 h in 40 sccm H₂ and then purged in 20 sccm Ar for 15 h without exposure to air. This temperature is lower than that used for the reactor studies due to the upper limit of the system used. However, temperature-programmed reduction (TPR) results presented here show no additional reduction features from 673-723 K. CO chemisorption was performed at 323 K using 1 mL injections of 20% CO in Ar. This temperature was chosen to ensure that any CO dosed would not adsorb onto the alumina surface [140] while remaining low enough to ensure no desorption would be expected from platinum [128], Mo [129], or Pt-Mo [148] sites. These injections were repeated until the intensity of the CO desorption peak remained constant within $\pm 0.5\%$, indicating that no additional CO was adsorbing.

Particle sizes were also measured using transmission electron microscopy (TEM) performed

on an FEI Tecnai G2 ST20 TEM operating at 200 kV. Particle size estimates were obtained using ImageJ software to analyze images, sampling at least 100 particles for each material.

TPR experiments were performed in a U-shaped quartz tube at atmospheric pressure. Approximately 100 mg of catalyst was held in the tube with quartz wool and pretreated at 723 K for 1 h in 40 sccm of 1% O₂ in He. The sample was then cooled to room temperature in He. 0.2 sccm H₂ and 20 sccm He were then flowed over the sample as the temperature was ramped linearly at 10 K/min to 1073 K with outlet gas monitored by a quadrupole residual gas analyzer (Stanford Research Systems model RGA 100).

Acid site characterization was performed using ammonia temperature-programmed desorption (TPD) in a reactor described in detail elsewhere. Approximately 12 mg of catalyst was loaded into a quartz tube (6.35 mm inner diameter) and reduced in-situ at 723 K for 1 h in 20 sccm H₂, 40 sccm He. The tube was then cooled under He flow to 373 K and three 1 mL injections of NH₃ (Airgas, anhydrous, 99.99%) were performed to ensure saturation of the catalyst. Then three 200 μ L injections of NH₃ were performed for use as a calibration for quantification of the resulting TPD. Desorption of ammonia was measured using a Pfeiffer mass spectrometer to track mass fragment $m/z=15$. The area under this peak was used to quantify acid site density by comparing it to the area of the calibration injections.

In-situ XAS was performed at Argonne National Laboratory at the Advanced Photon Source (APS) on beamline 10-BM, operated by the Materials Research Collaborative Access Team (MRCAT). Experiments were performed in a continuous flow reactor consisting of a quartz tube (2.54 cm OD, 25.4 cm length) sealed at each end with Kapton windows held in place by Ultra-Torr fittings with ball valves welded to each to allow gas flow through the tube. Catalysts were pressed into a cylindrical sample holder containing six wells to produce a self-supporting wafer. A K-type thermocouple (Omega) was placed against the catalyst sample holder to measure temperature. The sample loading was determined by calculating the weight of catalyst required to give an absorbance (μ x) of approximately 1.0 when possible. Spectra were collected in transmission mode using ionization chamber detectors that were optimized for maximum current while maintaining a

linear response range (ca. 10^{10} photons detected s^{-1}). To calibrate the energies, a third detector in series with the two ionization chambers was used to collect a foil reference spectrum simultaneously with each measurement. Before collecting the spectra, the sample was reduced in-situ at 723 K in hydrogen and then allowed to cool to room temperature. This reduction temperature was chosen based on literature precedent for successfully reducing PtMo catalysts [96]. TPR performed on these catalysts was also used to confirm that the chosen reduction temperatures were higher than the observed hydrogen uptake features.

Standard methods were employed to normalize and calibrate the energy of the X-ray absorption near-edge structure (XANES) spectra. The maximum of the first peak was used to calculate edge energies by taking the first derivative of the XANES spectrum while the energy of pre-edge features was determined by the maximum in the peak intensity. Linear combination fitting of the XANES was performed where possible to estimate the fraction of metal in different oxidation states. Standard data reduction techniques were used to fit the data using the software program WinXAS 3.1 [196]. The extended X-ray absorption fine structure (EXAFS) parameters were determined by a least square fit in κ or R-space (as labeled in the table of fits) of the κ^2 -weighted Fourier Transform (FT) data. Where possible, experimental phase shift and backscattering amplitude were determined using standards of known structure; Pt-Pt scattering was determined using Pt foil (12 Pt-Pt at 0.277 nm) and Mo-O scattering was determined using Na_2MoO_4 (4 Mo-O at 0.177 nm). Theoretical phase and amplitude functions for Pt-Mo and Mo-Pt scattering were calculated with FEFF6 [197] using a two atom calculation, calibrated to Pt foil and Mo foil respectively. The mean-square disorder refined in WinXAS ($\Delta\sigma^2$) reflects the difference in disorder of the nanoparticles relative to the references.

Vapor phase upgrading experiments were performed using approximately 10 to 50 mg of catalyst that was pressed and sieved to an agglomerated material of 0.125-0.15 mm diameter and diluted with approximately 1.5 g silicon carbide of similar size to ensure isothermal operation. The mixture was loaded into a 13 mm ID stainless steel reactor tube with the catalyst bed held in place by quartz chips. The catalyst was reduced in-situ at 723 K for 2 h in 95% H_2 (balance Ar). The

reactor was then cooled and purged at room temperature for at least 12 h in N_2 without exposure to air. Experiments were then performed at 0.5 MPa and 523 K with 12:1 molar ratio of H_2 :oxygenate. These reaction conditions were chosen to study HDO at relatively low temperature and pressure; it would be preferable to perform ex-situ CFP without additional heating or pressurization of the vapor. The hydrogen feed was pre-blended with an Ar internal standard. Oxygenates were fed as a liquid using an HPLC pump to a heated zone upstream of the reactor where they were vaporized prior to reaching the inlet. The weight-hourly space velocity (WHSV) was varied to obtain data points at varying conversion. Products from the reactor outlet were monitored using an online gas chromatography/mass spectrometry system equipped with flame ionization and thermal conductivity detectors (Agilent). Concentrations of each compound were identified and quantified using standards prepared with known concentrations of the relevant compounds. These standards were prepared at a minimum of three concentrations spanning the range of concentrations expected under reaction conditions. This allowed for identification of retention times as well as quantification of concentration. Product identification was further confirmed using the system’s built-in mass spectrometer. All data had a mass balance closure within $\pm 5\%$. Operation under rate-limited conditions was confirmed by changing the space velocity both by altering flow rates with the same catalyst mass and by loading a different mass of catalyst at the same reactant flows and noting that the results were the same. Internal mass transfer limitations were ruled out using the Weisz-Prater parameter, calculated to be approximately 0.02 [198, 199]. More detail on this calculation can be found in a previous report [9]. Conversion was calculated by dividing the moles of carbon-containing primary products formed by the total moles of these products and the remaining reactant measured in the outlet. For example, for m-cresol (C) upgrading, the products detected were methylcyclohexane (R), 3-methylcyclohexanol (OH), and 3-methylcyclohexanone (O). The conversion (X) was determined using Eq. (4.1) where N_i is the moles of compound i. Conversions were determined at steady state, after approximately 2 h on stream at the given condition. Rates were computed by multiplying the measured mol% of a given compound in the outlet and the total molar flow rate through the system. The water-free product selectivities reported were determined

on a molar basis by dividing the moles of a given species by the total moles of products formed. Weight hourly space velocity (WHSV) was calculated by dividing the mass flow rate of the reactant by the total mass of catalyst loaded.

$$X_C = \frac{N_R + N_{OH} + N_O}{N_C + N_R + N_{OH} + N_O} \quad (4.1)$$

A separate, atmospheric pressure tubular packed bed flow reactor optimized for measuring kinetics at low conversion was used for some experiments. Reactants were introduced by bubbling helium through the liquid reactant (either m-cresol or 3-methylcyclohexanol) that was immersed in a water bath at 333 K. The saturated He was then mixed with H₂ and diluent He before flowing over the catalyst bed. The reactor effluent was analyzed using an Agilent Technologies 7890A gas chromatograph with a 30 m 0.320 mm Agilent HP-5 (5% phenyl)-methylpolysiloxane capillary column and flame ionization detector.

4.2.2 Computational methods

All calculations used periodic DFT as implemented in the Vienna Ab initio Simulation Package 5.3.3 (VASP) [149, 150, 200, 201]. The ion-electron interactions were described using the projector augmented wave (PAW) potentials [120, 121] with an energy cutoff of 6.41×10^{-17} J for the plane wave basis set. The generalized gradient corrected Perdew-Burke-Ernzerhof (PBE) functional was used for all periodic calculations with Monkhorst-Pack 5x5x1 k-point sampling. Optimizations were carried out until the forces converged to 8.01×10^{-20} J/nm for geometry optimizations and 1.28×10^{-19} J/nm for nudged elastic band calculations using the quasi-Newton method for geometry optimization. The van der Waals (vdW) forces were calculated using the method of Tkatchenko and Scheffler as implemented in VASP [202, 203].

To understand the reactivity of m-cresol over pure Pt(111) and PtMo(111), models were constructed for each surface. Slab models were formed from the optimized platinum unit cell. The Mo was added to a Pt(111) surface by substituting a Mo atom for one of the Pt atoms. The slabs were otherwise unchanged. The slab geometries were generated using Atomic Simulation

Environment 3 (ASE). The optimized lattice vectors for the slab were $(11.247, 5.624, 0.000 \times 0.000, 9.741, 0.000 \times 0.000, 0.000, 30.000)$. The final vector allows for sufficient distance between slabs to avoid unphysical interactions between slabs. The surface models are five-layers thick with a stoichiometry of Pt_{80} and $\text{Pt}_{79}\text{Mo}_1$. The upper two layers were relaxed while the lower layers were fixed at their ideal crystal positions. The Mo atoms were included in the surface layer.

Previous ab initio thermodynamics studies indicate the Pt(111) surface would have a high coverage of hydrogen at the experimental temperature and pressure [204, 205]. Previous work with Pt and PtRe supported catalysts used for glycerol hydrogenolysis at 548 K reported that the reaction order with respect to hydrogen was zero, further suggesting that the surface is crowded under the experimental conditions used here. For these reasons, all of the calculations were started using a surface with complete hydrogen coverage or a single surface vacancy in the hydrogen monolayer. For the models including Mo, the vacancy was over the Mo site, as the hydrogen vacancy formation energy is zero at the Mo site. The full models including the reacting m-cresol are shown in Fig. 4.2. Barriers were determined using nudged elastic band calculations with 7-11 images in addition to the reactants and products. All energies were referenced to the preceding step with hydrogen adsorption energies neglected in the reference and at each step in the reaction. This model of a PtMo surface is not meant to replicate experimental results, but rather to provide an understanding of fundamental interactions driving reactivity by understanding the effect of Mo atoms that are interacting with Pt atoms.

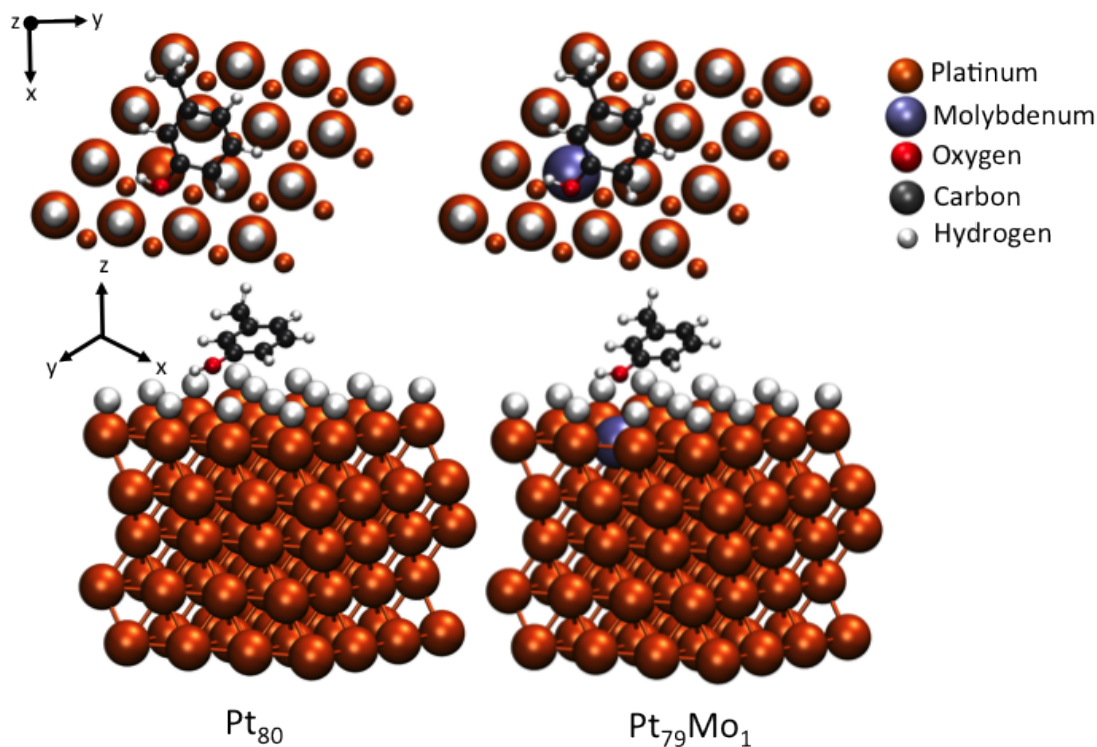


Figure 4.2: The models used for DFT calculations of the reaction network.

4.3 Results

4.3.1 m-Cresol HDO

The vapor phase upgrading of m-cresol was studied over Pt/Al₂O₃ and PtMo/Al₂O₃ catalysts. At 523 K, 0.5 MPa, and 12:1 H₂:m-cresol, the major products formed were methylcyclohexane (MCH), 3-methylcyclohexanol, and 3-methylcyclohexanone over all materials, shown in Fig. 4.1. Benzene and toluene were observed in trace amounts (less than 0.5 mol%). No transmethylation reactions were observed, consistent with a prior report [206]. At approximately 10% conversion the rate of product formation in units of mmol·min⁻¹·g catalyst⁻¹ was 6 over Pt, 4 Pt₁₀Mo₁, and 3 over Pt₁Mo₁. Using the CO chemisorption data presented in the characterization section below to estimate the moles of exposed sites, these rates correspond to turnover frequencies (TOF) of 0.76, 0.65, and 0.68 s⁻¹ over Pt, Pt₁₀Mo₁, and Pt₁Mo₁ respectively. Activity trends are

further analyzed below.

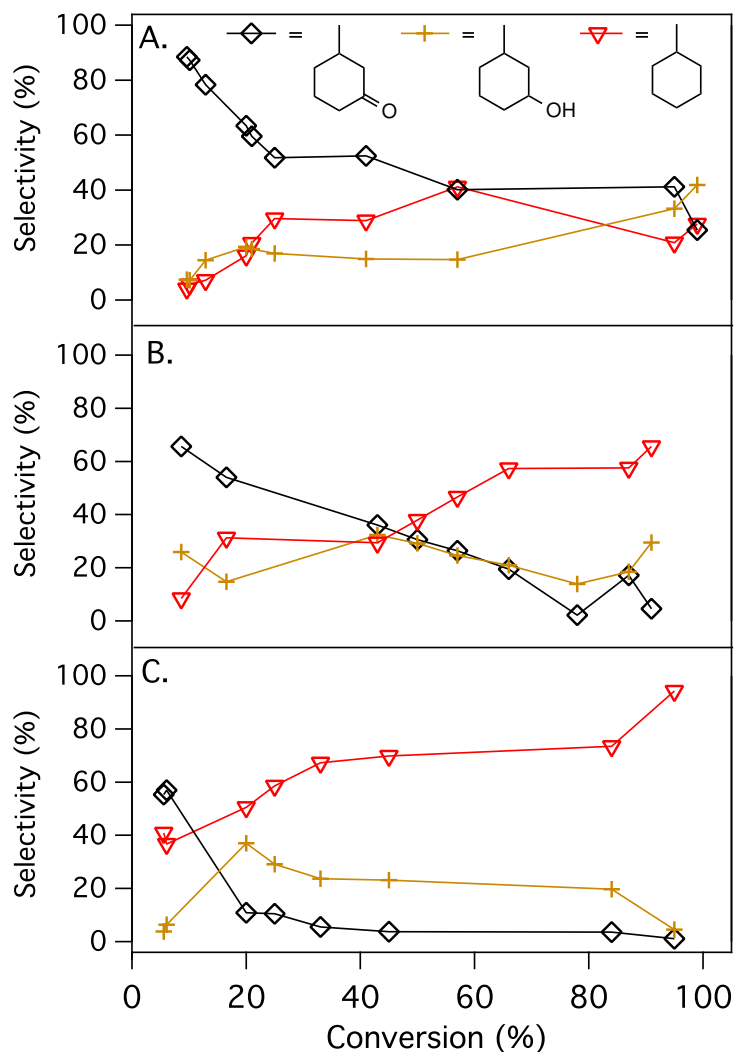


Figure 4.3: Selectivities at 523 K, 0.5 MPa for 3-methylcyclohexanone (black diamonds), 3-methylcyclohexanol (gold crosses), and methylcyclohexane (red triangles) production from m-cresol HDO over alumina-supported A. Pt, B. Pt₁₀Mo₁, and C. Pt₁Mo₁

The product selectivities measured as a function of conversion are reported in Fig. 4.3. The selectivity to 3-methylcyclohexanone was highest over monometallic Pt, whereas the bimetallics had a greater selectivity towards 3-methylcyclohexanol and MCH, especially Pt₁Mo₁. In addition to higher deoxygenation selectivity, the bimetallic catalysts showed higher activity for MCH production. Over Pt, Pt₁₀Mo₁, and Pt₁Mo₁ respectively the rates of MCH production at

approximately 20% conversion were 0.4, 20, and 10 mmol-min⁻¹-g catalyst⁻¹. The alcohol:ketone ratio observed experimentally over the metal/alumina catalysts was lower than the equilibrium value of 3.5, especially at lower conversions, consistent with there being a kinetically relevant barrier for ketone hydrogenation during these experiments. These ratios can be seen in Table 4.1. On the monometallic Pt/Al₂O₃ catalyst, the selectivity toward 3-methylcyclohexanone approached 100% at low conversion, suggesting that the other reaction products observed at higher conversion were formed in series from this primary product, as shown in Fig. 4.1a. This is consistent with previous work indicating that HDO on Pt/Al₂O₃ catalysts involves sequential hydrogenation and dehydration steps, with dehydration being attributed to acid sites on the catalyst support [31, 36, 72, 207–209]. To confirm that dehydration was occurring over the support in the experiments reported here, the intermediate product 3-methylcyclohexanol was fed over pure alumina under the same reaction conditions (523 K, 0.5 MPa total pressure, 12:1 H₂:alcohol, and the same range of space velocities). For 3-methylcyclohexanol conversions of 25-70%, the product stream was 96-99 mol% methylcyclohexene, the alkene product formed from dehydration of the saturated alcohol. The balance was 3-methylcyclohexanone, formed through alcohol dehydrogenation.

Table 4.1: Experimental alcohol:ketone ratios from the selectivity data plotted in Fig. 4.3. For comparison, the calculated equilibrium value of alcohol:ketone is 3.5.

Pt/Al ₂ O ₃		Pt ₁₀ Mo ₁ /Al ₂ O ₃		Pt ₁ Mo ₁ /Al ₂ O ₃	
Conversion (%)	alcohol:ketone	Conversion (%)	alcohol:ketone	Conversion (%)	alcohol:ketone
10	0.08	9	0.40	6	0.11
13	0.18	17	0.27	20	3.39
20	0.31	43	0.90	25	2.78
21	0.31	50	0.95	33	4.33
25	0.33	57	0.93	45	6.19
41	0.28	66	1.08	84	5.52
57	0.37	78	6.29	95	4.22
95	0.81	87	1.08		
99	1.65				

Another test for the role of the support in HDO of cresol is to employ a support with a low acid site concentration. We therefore tested Pt/C for reaction of cresol at the same conditions. As the carbon supports have low activity for dehydration [38], the reactivity should result from the

metal sites. Selectivity toward MCH was observed to be very low over the Pt/C catalysts, even at high conversion. Thus, the results for the pure Pt/Al₂O₃ catalyst can largely be understood in terms of a sequence of hydrogenation reactions on Pt and deoxygenation reactions on the support, though we note that behavior at high conversions in Fig. 4.3 appears to be complex.

Mo-containing catalysts exhibited much higher selectivities and rates for MCH formation, i.e. Mo served to provide additional deoxygenation activity that augmented the activity of acid sites on the support. As shown in Fig. 4.4, a Pt₁Mo₁/C catalyst demonstrated significant MCH production without requiring acidic sites on the support. Using an Al₂O₃ support for Pt₁Mo₁ resulted in even higher MCH selectivities. Thus, one possible explanation for the enhanced MCH rate and selectivity over Mo-containing catalysts is that Mo sites simply provide additional acid sites, acting to augment those provided by the support. Ammonia TPD experiments were performed over Pt/Al₂O₃ and Pt₁Mo₁/Al₂O₃ to investigate this possibility. Less acidity was measured on the bimetallic catalyst; the acid site density over Pt was measured to be 391 ± 38 $\mu\text{mol/g}$ catalyst and over Pt₁Mo₁ was 214 ± 43 $\mu\text{mol/g}$ catalyst (error bars represent the standard deviation based on the average of three separate samples). We note that this measurement does not distinguish between types of acid sites, and the drop in overall measured acid site density with Mo content is not reflected in the near-constant rate of MCH formation from 3-methylcyclohexanol discussed above. However, these results do suggest that addition of Mo does not result in a large increase in acid site concentration. Furthermore, it is important to note that the selectivity as a function of conversion profiles for the bimetallic catalysts differ significantly from their monometallic counterpart. In particular, the selectivity to MCH was approximately 40% on the Pt₁Mo₁/Al₂O₃ catalyst even at <10% conversion. This high selectivity at low conversion indicates a possible parallel path for formation of MCH (i.e., one that does not involve initial methylcyclohexanone formation), as in the mechanism shown in Fig. 4.1d. We therefore hypothesize that there are two mechanisms responsible for MCH formation on PtMo/Al₂O₃ catalysts. Because the catalyst still contains active Pt hydrogenation sites and acid sites on the support, the sequential hydrogenation/dehydration mechanism is still possible. In addition, however, we propose that the presence of Mo sites enables an additional

pathway that does not require initial saturated ketone formation.

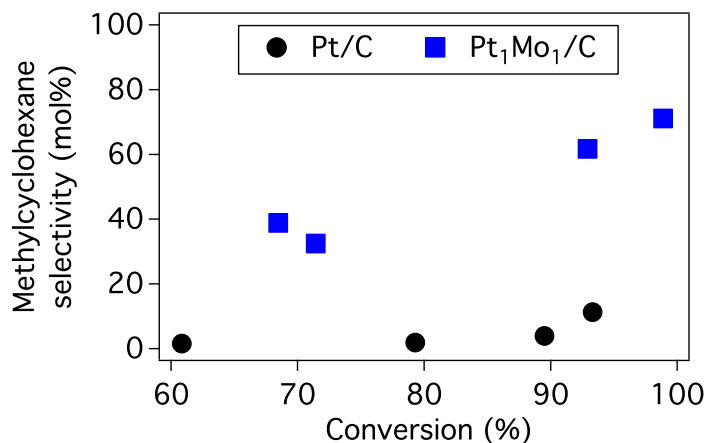


Figure 4.4: Selectivities at 523 K and 0.5 MPa for MCH production from m-cresol HDO over carbon supported Pt and Pt₁Mo₁.

We conducted various control experiments to test this hypothesis. For example, we tested the Pt₁Mo₁/C catalyst in a separate flow reactor optimized for measuring kinetics at low conversion. Note that this low-conversion reactor operated at much lower total pressure and reactant concentration, leading to quantitative differences in activity and selectivity; however, as discussed below, the trends in selectivity were preserved. At a conversion of less than 2%, the MCH selectivity was measured to be 22%. This result suggests that a portion of the deoxygenation activity originates from a reaction that is parallel to the production of methylcyclohexanone. However, note from Fig. 4.4 that selectivity does improve with conversion, even in the absence of an active support. This may indicate a series component to the production of MCH on the bimetallic, or alternatively to kinetics for competing reactions that vary with gas composition.

We also measured the rates of 3-methylcyclohexanol dehydration over the three catalysts (Table 4.2) to focus on the dehydration step. In contrast to the results with m-cresol, there was little change in the deoxygenation rate. This suggests that MCH production from 3-methylcyclohexanol occurs mainly via reaction on acidic sites on the alumina, which are assumed to have approximately equal abundance on all the catalysts due to the similar surface areas of each metal (Table 4.3).

Thus, Mo appears to affect a different step in the overall reaction mechanism for cresol.

Table 4.2: Rate of MCH production from the reaction of 12:1 H₂:3-methylcyclohexanol at 523 K, 0.1 MPa

Catalyst	rate ($\mu\text{mol alkane s}^{-1} \text{ g cat}^{-1}$) ^a	Conversion (%)
Pt/Al ₂ O ₃	37.2 $\pm$ 0.4	20
Pt ₁₀ Mo ₁ /Al ₂ O ₃	38.0 $\pm$ 0.4	25
Pt ₁ Mo ₁ /Al ₂ O ₃	37.9 $\pm$ 0.4	17
^a Error ranges indicate the standard deviation in 3-5 repeated measurements of product concentration		

Addition of Mo to the Pt catalysts affected not only the steady state catalyst performance, but also the behavior as a function of time on stream. Fig. 4.5 shows time on stream data for low conversion of m-cresol over each catalyst. Note that with increased Mo content, a longer time was required to achieve a nearly steady reaction rate. The evolution of the PtMo structure with exposure to reaction conditions appears to be complex, and is the subject of ongoing investigations in our laboratories.

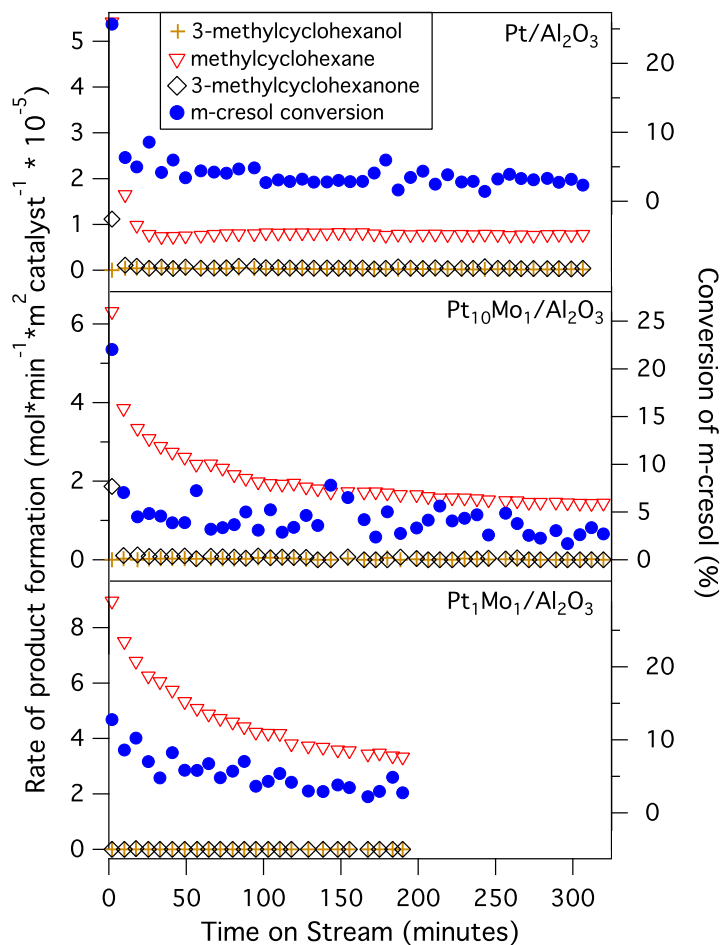


Figure 4.5: Rates of production formation (left axis) and conversion (right axis) as a function of time on stream at 523 K, atmospheric pressure for 3-methylcyclohexanone (black diamonds), 3-methylcyclohexanol (gold crosses), and methylcyclohexane (red triangles) production from m-cresol HDO over alumina-supported Pt (top panel), Pt₁₀Mo₁ (center panel), and Pt₁Mo₁ (bottom panel). The molar ratio of H₂:m-cresol in feed was 21:1 with a mole fraction of 0.28 H₂, 0.001 m-cresol, and the balance He.

4.3.2 Reaction network

DFT calculations were performed on models of the hydrogen covered Pt and PtMo surfaces (Fig. 4.2) to evaluate mechanisms by which PtMo catalyzes m-cresol deoxygenation. Mechanisms that have previously been proposed for HDO over a variety of catalysts (Fig. 4.1) were investigated to find the lowest barrier pathway over the surfaces studied here. The models used in these studies are intended to elucidate trends in the reactivity rather than to be exact representations of the

experimental catalysts. There are several possible mechanisms of m-cresol deoxygenation over the Pt surface, as shown in Fig. 4.1. The two pathways studied here (ring hydrogenation and tautomerization followed by deoxygenation) were investigated to determine if the inclusion of Mo in the Pt(111) surface could alter the deoxygenation pathway. The reaction network including these two mechanisms along with calculated reaction energies and barriers are presented in Fig. 4.6. The calculations performed over Pt(111) without Mo inclusion are also reported in a previous study [72]. The computed ring hydrogenation mechanism is shown in Fig. 4.6A.

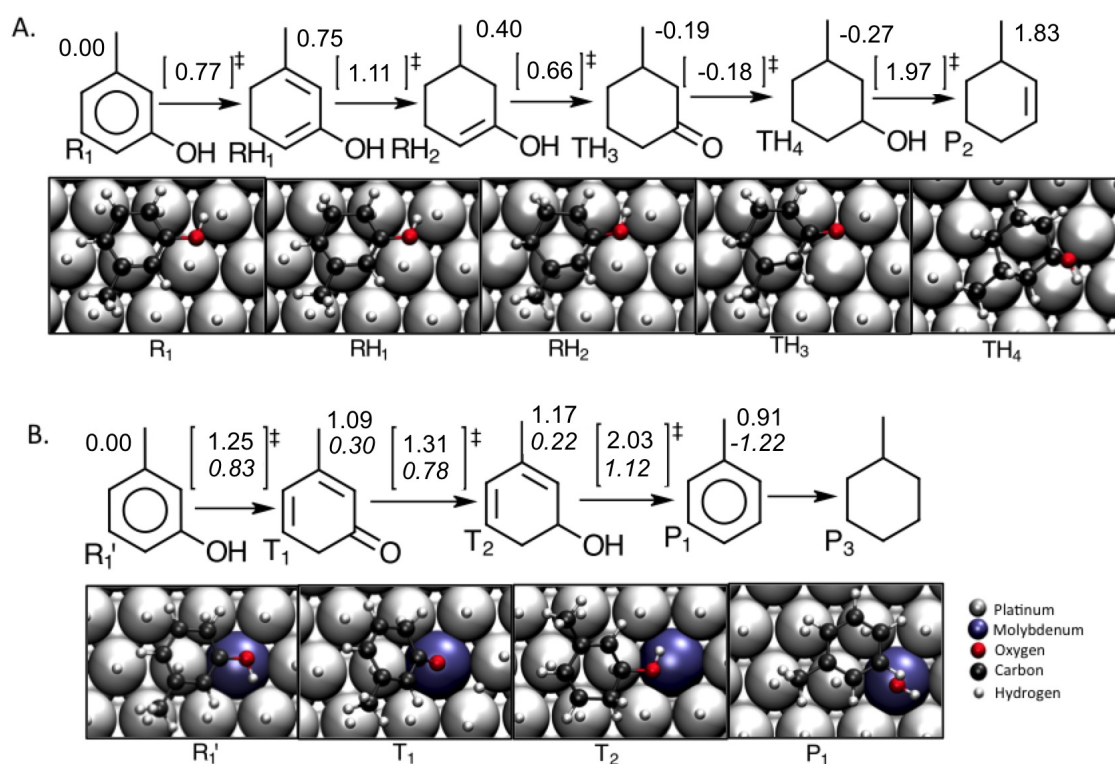


Figure 4.6: The reaction network calculated for direct ring hydrogenation on H/Pt(111) shown in pathway A and tautomerization shown over both monometallic and bimetallic surfaces in pathway B. All values are in $\text{J} \times 10^{-19}$. In pathway B the values in italics are reaction energies and barriers over the Mo site in the H/Pt(111) surface and the values in plain text are the corresponding value on an unmodified H/Pt(111) surface. Important minima are represented by ball and stick models with the designation corresponding to the reaction networks. Reaction barriers are denoted in brackets with a $\ddagger$ and other reported values are reaction energies.

The ring hydrogenation pathway was examined starting from a surface covered with a

complete hydrogen monolayer. The first step in the pathway is hydrogenation of the aromatic carbon-carbon bond, shown in step R_1 to RH_1 , which has a barrier of 7.69×10^{-20} J. This step is endothermic by 7.53×10^{-20} J and occurs as a simultaneous transfer of two H atoms. This is in contrast to the hydrogenation occurring as two single hydrogen transfer steps as has been shown over the surface without hydrogen coverage [49, 191, 209–211]. The change in reactivity with hydrogen coverage has been previously observed for furfural reacting on the Pd(111) surface [157]. In this work, the structure resulting from a single hydrogen transfer was not a minimum on the potential energy surface. Geometry optimization starting from the single hydrogen-transfer structure results in spontaneous transfer of the second hydrogen to form the final product, or else the optimization results in the reactant. The next step in the reaction is the conversion from RH_1 to RH_2 , which is the highest energy point in the reaction pathway. The following step is a keto-enol tautomerization to form TH_3 , which can subsequently be hydrogenated to form the alcohol. Direct removal of the hydroxyl group from structure TH_4 is significantly endothermic by 1.83×10^{-19} J and has a barrier of 1.97×10^{-19} J. As the energies of TH_3 and TH_4 are equivalent, a distribution of these species would be predicted as desorption products. While deoxygenation is unlikely via pathway A on the Pt(111) surface, deoxygenation over the acidic alumina support to form the aromatic product labeled P_1 is most likely the major route for deoxygenation. This may then be followed by hydrogenation to P_3 to produce the saturated alkane. Fig. 4.6A only shows direct ring hydrogenation for Pt(111); adsorption of H atoms on Mo sites was found to be unfavorable as these sites strongly prefer to interact with the oxygen atom. Therefore, direct ring hydrogenation on PtMo is expected to occur over Pt sites in a similar fashion to that on the unmodified H/Pt(111) surface, as shown in Fig. 4.6A.

The mechanism shown in Fig. 4.6B, first proposed by Nie and Resasco [52], begins with tautomerization of the m-cresol into the keto-intermediate followed by deoxygenation. Ring hydrogenation is also possible but is considered elsewhere [72]. In this mechanism, the reaction is a concerted H-transfer, as shown in Fig. 4.7. One H transfers from the surface to the m-cresol ring and the second H transfers from the m-cresol hydroxyl group to the surface.

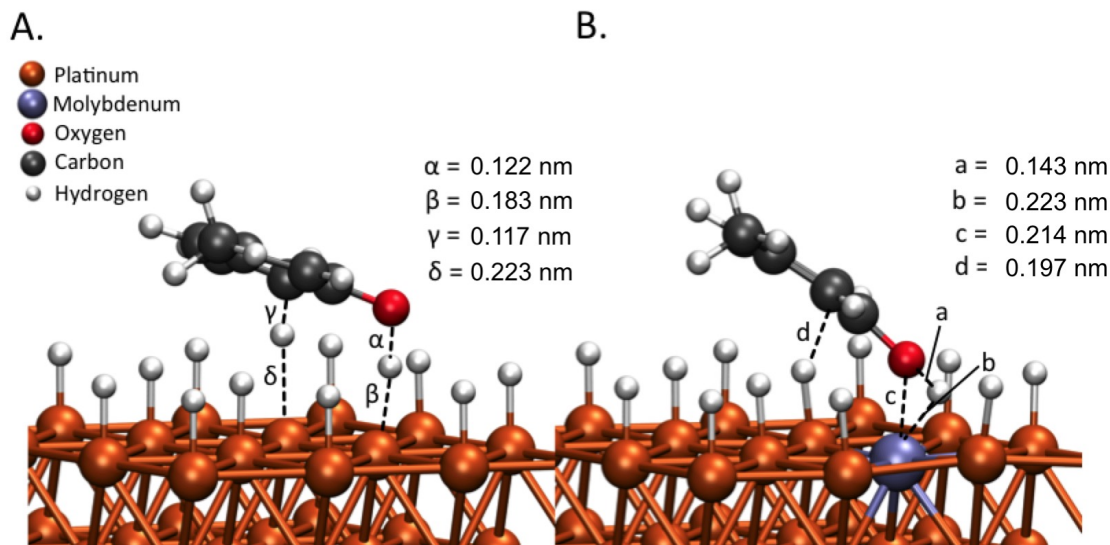


Figure 4.7: The geometry of the transition state with bond distances indicated for the tautomerization step $R_1'-T_1$ over the Pt(111) surface A. and the Pt(111) surface with Mo substitution B.

The energetics for this tautomerization reaction, shown by the step from R_1' to T_1 in Fig. 4.6B, indicate a significant difference between the Pt and PtMo surfaces. The difference of 4.17×10^{-20} J for the barrier and 7.85×10^{-20} J for the reaction energy indicates a significant effect of the Mo on this reaction step. This energetic change is due to the stronger O-Mo interaction in the transition and final states. In the transition state structure for Pt(111) in Fig. 4.7A, the oxygen does not directly interact with the surface, while in the transition state for the bimetallic surface (Fig. 4.7B), the oxygen directly interacts with the surface Mo. The Mo inclusion significantly reduces the oxygen-surface distance from 0.305 nm to 0.214 nm. Thus if Mo is present, surface-assisted tautomerization would become more favorable. This additional deoxygenation pathway agrees with experimental results showing increased deoxygenation rates over bimetallic catalysts (Fig. 4.5). At less than 5% conversion, the steady state rates of alkane production from m-cresol HDO over Pt/ Al_2O_3 , $\text{Pt}_{10}\text{Mo}_1/\text{Al}_2\text{O}_3$, and $\text{Pt}_1\text{Mo}_1/\text{Al}_2\text{O}_3$ were approximately 8×10^{-6} , 1.5×10^{-5} , and 3.5×10^{-5} mol-min $^{-1}$ -m $^{-2}$ catalyst respectively.

After tautomerization, deoxygenation occurs in step T_2 to P_1 , breaking the aryl-O bond. The

barrier to this step is significantly lower (1.12×10^{-19} J vs. 2.03×10^{-19} J) with Mo included in the Pt(111) lattice. Toluene was not observed as a product; however, thermodynamic equilibrium under the conditions in this study significantly favors MCH. The equilibrium ratio of MCH to toluene was calculated to be 320 at 523 K. This is consistent with previous studies of aromatic hydrogenation, which has been shown to be fast over Pt catalysts at comparable temperatures. For example, toluene hydrogenation over 10 wt% Pt/ Al_2O_3 at 573 K had a TOF of 139.8 s^{-1} [212]. Previous reports of toluene production from m-cresol HDO at high H_2 :m-cresol ratios were for reactions performed at 573 K [49, 52]. This reaction temperature increase of 50 K dramatically impacts the calculated thermodynamic equilibrium ratio of MCH to toluene, lowering it from 320 to 4. If the overall mechanism is considered, the minimum energy pathway is ring hydrogenation over the Pt(111) surface with an additional mechanism of tautomerization followed by deoxygenation possible over the PtMo surface. This agrees with the experimental results in Fig. 4.3, which suggest that the ketone is a primary product over both Pt and PtMo surfaces due to the lowest energy pathways beginning with a hydrogenation or hydrogen transfer step.

The final step probed by DFT calculations is the formation of water from a surface-adsorbed hydroxyl group. As Mo sites have stronger interactions with oxygen, it is possible that water formation could become rate limiting. To evaluate this hypothesis, the barrier to water formation was calculated over the Pt(111) and PtMo surfaces. Over the PtMo surface, the barrier to water formation was 5.61×10^{-20} J and was exothermic by 4.97×10^{-20} J, while the barrier for the Pt surface was 1.76×10^{-20} J and was exothermic by 1.25×10^{-19} J. Based on these results, this reaction step is not rate limiting.

4.3.3 Catalyst characterization

To correlate catalyst performance with structure, including the simulated structures in the previous section, characterization efforts were focused on determining the state and distribution of the Mo on the bimetallic catalyst. TPR was used to characterize carbon- and alumina-supported Pt, Mo, and PtMo samples, with the results shown in Fig. 4.8. The monometallic Pt/ Al_2O_3

catalyst showed two hydrogen uptake features, one at 490 K and a higher temperature peak at 650 K. The reduction at 490 K is consistent with previous TPR results for Pt/ Al_2O_3 catalysts, and a smaller feature at higher temperature is also frequently reported [30, 213, 214]. This latter feature is often attributed to a strong interaction with the support, but may also be the reduction of under-coordinated sites such as steps and edges on some of the particles. TPR performed on Pt/C catalysts also demonstrated more than one reduction feature for catalysts with low weight loadings (<1 wt%) [215, 216]. Previous studies reporting a series of TPR profiles of Pt/ Al_2O_3 catalysts with different metal loadings showed peaks around 490 K and 650 K with lower wt% Pt [214]. For the lowest metal loadings, these two peaks were comparable in size. However, as the metal loading was increased (i.e., decreasing the relative concentration of defect sites), the lower temperature peak dominated. At the highest metal loadings, the high temperature reduction feature was no longer observed.

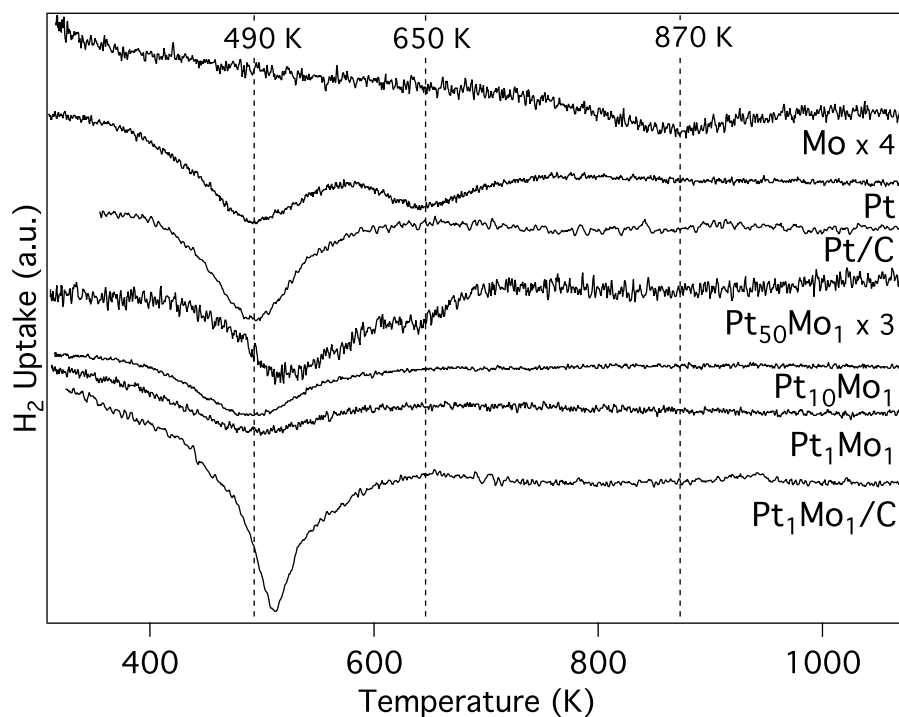


Figure 4.8: TPR profiles for Pt, Mo, and PtMo catalysts. Samples are supported on alumina unless otherwise noted. All signals are normalized to mass of catalyst loaded and mass spectrometer pressure.

In the present study, we observed that as Mo was added to the Pt catalyst, the high-temperature TPR feature disappeared. This peak was not detected for Mo loadings with a Pt:Mo atomic ratio less than 50:1. Thus, addition of Mo (which forms strong metal-oxygen bonds) to Pt actually decreases the fraction of sites that require high temperature to reduce. This may be attributable to Mo increasing the average particle size of the catalyst, thus decreasing the fraction of small particles with large concentrations of step and edge sites. Addition of Mo has previously been shown to decrease the dispersion of supported Pt catalysts [126]. TEM images (Fig. 4.9) show slightly larger average particle sizes for the PtMo bimetallic catalysts. Note that monometallic Mo/ Al_2O_3 exhibited reduction features above 800 K that were not observed in the PtMo catalysts. Mo sites on the PtMo catalysts are likely reduced through a spillover effect, where Pt is responsible for activating H_2 that then migrates to Mo sites. This spillover effect has often been suggested for bimetallic catalysts containing a hydrogenation metal, including previous work with PtMo [217]. The $\text{Pt}_{10}\text{Mo}_1$ and Pt_1Mo_1 bimetallic catalysts used here also did not show reduction peaks around 850-870 K as seen on monometallic Mo, suggesting there is sufficient mixing of the two metals to prevent large domains that act as bulk Mo or Mo oxides. This is expected to be advantageous for catalytic activity because previous surface science investigations of Mo-modified Pt(111) have shown that reduced Mo has a significant effect on surface reactivity, whereas oxidized Mo mainly serves to block active sites [148].

CO chemisorption was used to estimate the active surface area of each catalyst. The results can be seen in Table 4.3. As the Mo loading increased, the measured surface area of the catalyst decreased. Previous CO-TPD studies on pure alumina show desorption temperatures less than 200 K, so that CO adsorption is expected to measure only the exposed metal sites [140]. While our previous work with PtMo surfaces under ultra-high vacuum (UHV) conditions showed decreased CO adsorption energy on reduced PtMo bimetallics, the expected desorption temperatures were still higher than 425 K [148]. This suggests the decrease in CO uptake was due to a decreased active surface area. This could be due to the increased total metal loading as catalysts with higher weight percent metal tend to result in larger particle sizes [31, 218, 219]. These TPR and CO

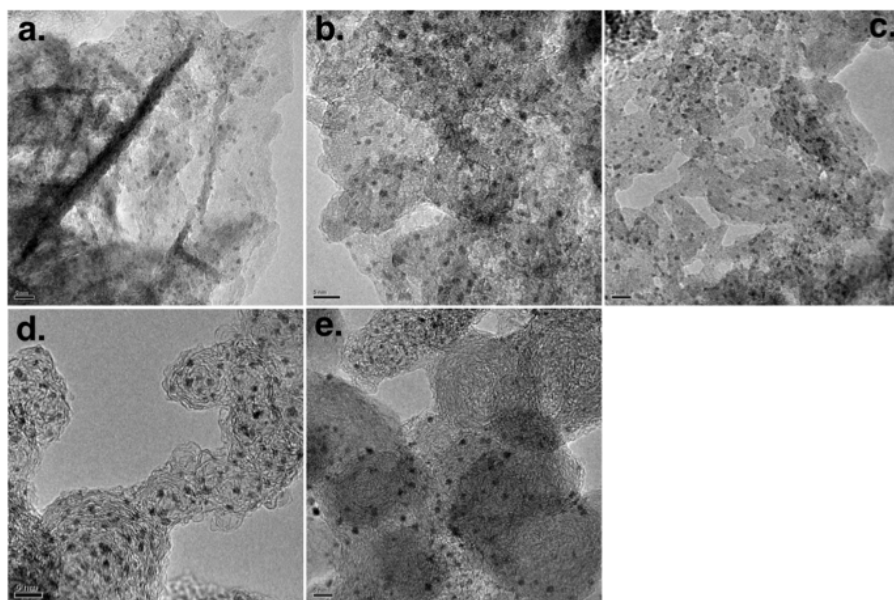


Figure 4.9: TEM images of a.) Pt/Al₂O₃, b.) Pt₁₀Mo₁/Al₂O₃, c.) Pt₁Mo₁/Al₂O₃, d.) Pt/C, and e.) Pt₁Mo₁/C. TEM was performed on an FEI Tecnai G2 ST20 TEM operating at 200 kV.

chemisorption results suggest that the PtMo catalysts had fewer exposed active sites than the monometallic Pt sample.

Table 4.3: TEM estimated particle sizes and CO chemisorption results for estimating dispersion and surface area of Pt and PtMo catalysts, reported with a 95% confidence interval

Catalyst	Weight % Pt (from ICP) ^a	Weight % Mo (from ICP) ^a	Dispersion (%)	CO uptake ($\mu\text{mol CO g cat}^{-1}$)	Active surface area ($\text{m}^2 \text{ g cat}^{-1}$)	Particle diameter (nm) ^b
Pt/Al ₂ O ₃	5.77	-	48.7 $\pm$ 2.5	125 $\pm$ 6	6.0 $\pm$ 0.3	1.25 $\pm$ 0.05
Pt ₁₀ Mo ₁ /Al ₂ O ₃	5.02	0.300	33.5 $\pm$ 1.3	95 $\pm$ 4	4.5 $\pm$ 0.2	1.31 $\pm$ 0.06
Pt ₁ Mo ₁ /Al ₂ O ₃	5.07	1.77	16.5 $\pm$ 0.7	82 $\pm$ 6	3.9 $\pm$ 0.1	1.60 $\pm$ 0.06
^a 95% confidence interval from replicate ICP results indicated an error less than 0.01%						
^b Measured from TEM images. 95% confidence intervals obtained from sampling >120 particles.						

X-ray absorption spectroscopy (XAS) was performed to further investigate the interaction between Pt and Mo in these catalysts. Experiments were performed on Pt/Al₂O₃, Pt₁₀Mo₁/Al₂O₃, and Pt₁Mo₁/Al₂O₃. The Pt L₃-edge XANES spectra and the Fourier-Transform of the Pt L₃-edge EXAFS spectra can be seen in Fig. 4.10. Reference spectra can be found in Fig. 4.11.

The shape and height of the white line of the XANES at the Pt edge is similar to Pt foil,

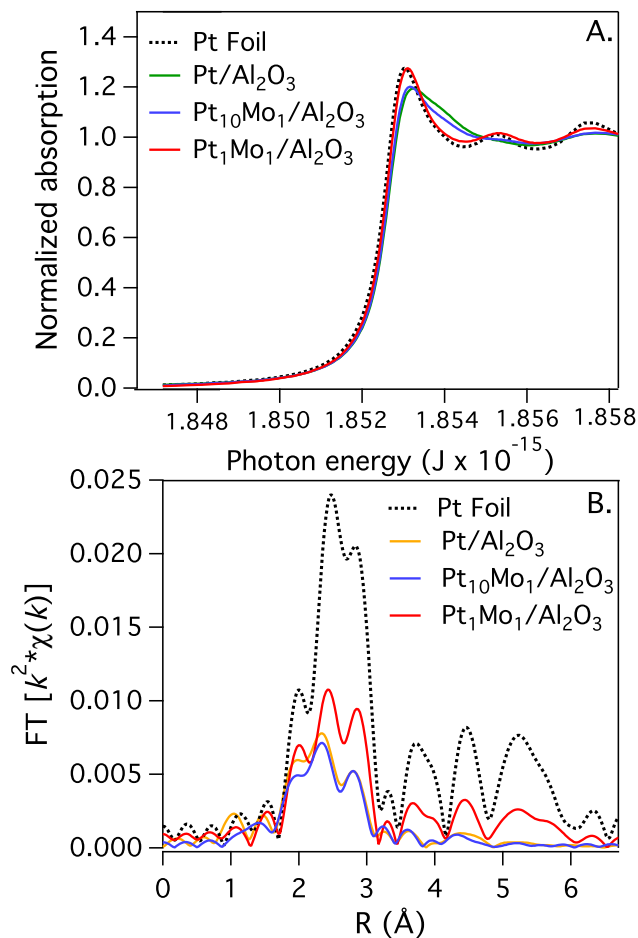


Figure 4.10: Pt L₃-edge XANES spectra of Pt and PtMo catalysts (A) and magnitude of the Fourier-Transform of the Pt L₃-edge EXAFS spectra of Pt and PtMo catalysts (B). All spectra taken at room temperature after pretreatment at 723 K in H₂.

indicating that all catalysts contained metallic Pt after reduction. Interestingly, the Pt₁Mo₁ white line intensity was similar to the Pt foil, while Pt₁₀Mo₁ was similar to Pt/Al₂O₃. This is potentially due to the larger particle size of Pt₁Mo₁; the effect of particle size on white line intensity was previously modeled using the assumption that charge transfer was negligible [220]. Though alloying could also affect the d-band density, which in turn affects the XAS white line intensity, this effect may be negligible in this case. The Fourier-Transform of the Pt L₃-edge EXAFS spectra is also shown in Fig. 4.10. Note the much higher amplitude of the foil (with 12 well-ordered Pt first neighbors and higher shell Pt neighbors). The Pt₁Mo₁/Al₂O₃ sample had larger higher shells than

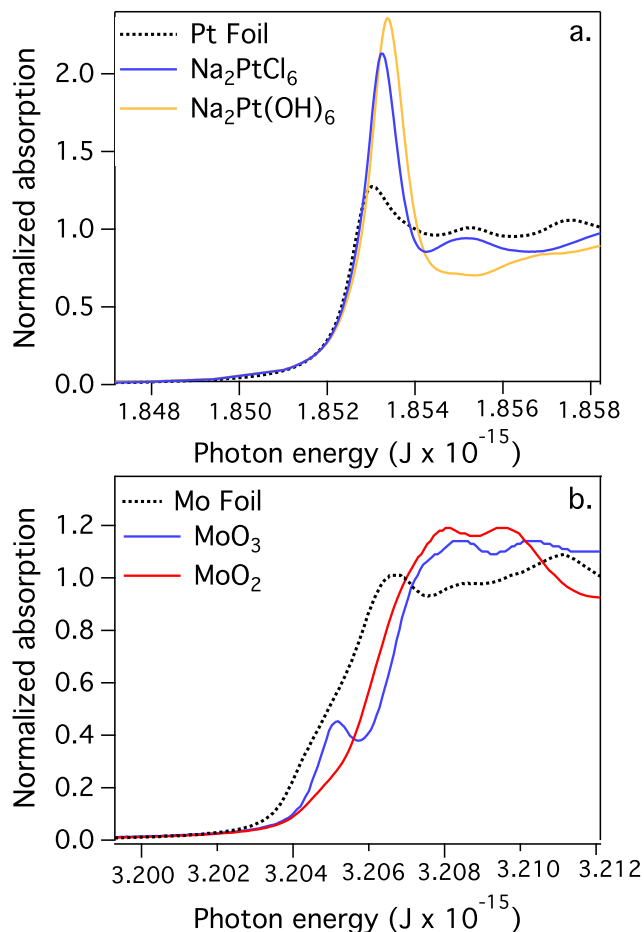


Figure 4.11: Pt L₃-edge XANES spectra of Pt references collected at room temperature after pretreatment at 723 K in H₂ (left) and Mo K-edge XANES spectra of Mo references in different oxidation states collected at room temperature with no hydrogen exposure (right).

the Pt₁₀Mo₁/Al₂O₃ sample, suggesting a catalyst with larger, more well-ordered metallic particles. A summary of the Pt L₃-edge XANES and EXAFS from R-space fitting can be found in Table 4.4.

The Pt edge EXAFS presented in Fig. 4.10 shows significant differences between Pt and PtMo samples. The low Pt-Pt coordination numbers found in the monometallic platinum and the Pt₁₀Mo₁ catalysts (7.4 and 6.7 respectively, as compared to 12 for a Pt foil) indicates that very small Pt particles are present. This is further supported by the contraction of the bond distances from 0.277 nm in the foil to only 0.271 nm for monometallic Pt and 0.270 nm for Pt₁₀Mo₁. Using previously established correlations between dispersion and coordination number [222], the estimated particle

Table 4.4: Summary of Pt L₃-edge XANES and EXAFS results from R-space fitting. Fitting range; κ^2 : $\Delta\kappa = 0.27$ - 1.21 nm^{-1} ; $\Delta R = 0.170$ - 0.310 nm . CN = coordination number; R = bond distance; $\Delta\sigma^2$ = mean-square disorder in the distribution of interatomic distances; ΔE_0 = energy offset. Samples were pre-treated in flowing H₂ at 723 K and measured in H₂ at RT. The estimated errors are: CN, ± 1 and R, $\pm 0.002 \text{ nm}$, within those typical for EXAFS fitting [221].

Sample	Edge energy (J $\times 10^{-15}$)	Scattering path	CN	R (nm)	$\Delta\sigma^2$ (nm ²)	ΔE_0
Pt foil	1.85277	Pt-Pt	12.0	0.277	N/A	N/A
Pt/Al ₂ O ₃	1.85281	Pt-Pt	7.4	0.271	0.00005	-4.5
Pt ₁₀ Mo ₁ /Al ₂ O ₃	1.85282	Pt-Pt	6.7	0.270	0.00005	-4.0
Pt ₁ Mo ₁ /Al ₂ O ₃	1.85281	Pt-Pt	8.0	0.275	0.00002	-1.2
		Pt-Mo	0.8	0.273	0.00002	10.8

size for these two samples is 1-2 nm. The Pt₁Mo₁ catalyst is estimated to have slightly larger particles, approximately 3 nm, due to the higher coordination number (8.0) and longer Pt-Pt bond distances (0.275 nm). This is in agreement with the trend shown from CO chemisorption results reported in Table 4.3, which also indicated slightly larger particle sizes with increasing Mo loading. It is also consistent with the particle sizes measured using TEM (see Fig. 4.9). These particle size trends from the EXAFS results further support the hypothesis that increased particle size could contribute to the disappearance of the high temperature reduction feature on bimetallic catalysts as seen in TPR. The relatively high Pt-Pt coordination number and low Pt-Mo coordination number indicates that there may be some Mo present as an oxide on the surface and/or that there may be a higher concentration of Mo near the surface of metal nanoparticles [223, 224]. However, it should also be noted that uncertainties in the coordination numbers limit the detail with which a precise bimetallic structure can be identified.

Only Pt-Pt scattering could be fit on the Pt₁₀Mo₁ sample due to the low concentration of Mo. However, the Pt₁Mo₁ had a stronger signal intensity and Pt-Mo scattering was also detected, indicating formation of bimetallic particles. The Pt-Pt scattering was 10 times larger than Pt-Mo, indicating the particles were Pt rich or that Mo segregated within the particles. Since there were only small Pt-Mo contributions, the higher shells were fairly unchanged relative to the foil due to the small perturbation to the structure.

The Mo K-edge was also studied and analyzed; the Mo K-edge XANES spectra and Fourier

Transform of the EXAFS data can be seen in Fig. 4.12. Reference spectra can be found in Fig. 4.11. No Mo-Mo scattering was observed (Table 4.5), indicating that Mo is most likely not forming aggregates within the bimetallics. These nanoparticles are expected to be a kinetically trapped bimetallic structure rather than a true bulk alloy. PtMo alloys do exist, but require annealing to over 1073 K [225].

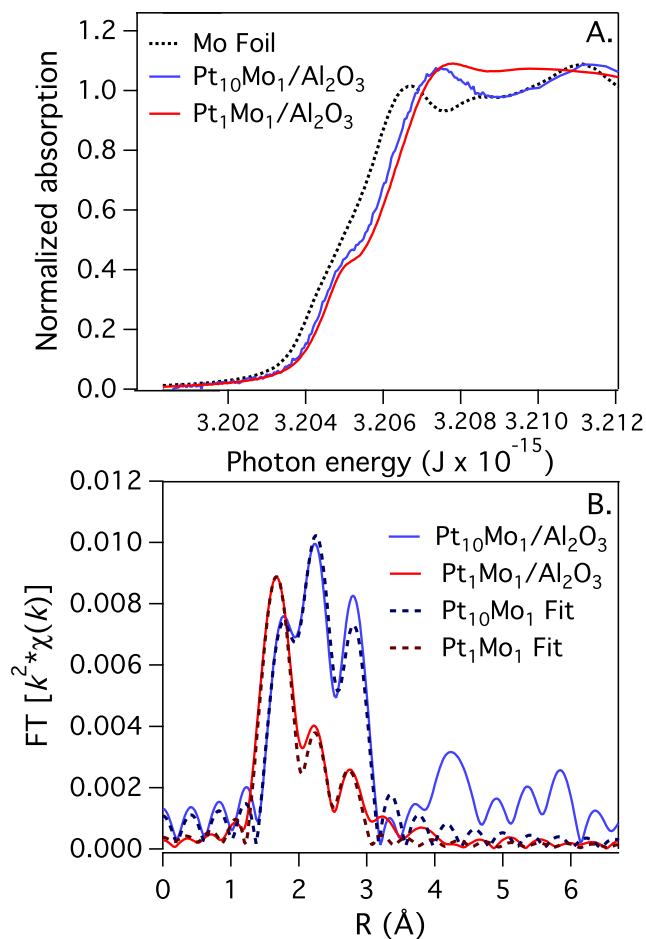


Figure 4.12: Mo K-edge XANES spectra of PtMo catalysts (left) and magnitude of the Fourier-Transform (non-phase shift corrected) of the Mo K-edge EXAFS spectra of PtMo catalysts collected at room temperature after pretreatment at 723 K in H₂.

The XANES spectra in Fig. 4.12 suggest that both Pt₁₀Mo₁/Al₂O₃ and Pt₁Mo₁/Al₂O₃ contain a mixture of reduced and oxidized Mo. The Fourier-Transform of the Mo K-edge EXAFS spectra shows a much larger Mo-Pt correlation in the Pt₁₀Mo₁/Al₂O₃ sample compared to the

Pt₁Mo₁/Al₂O₃ sample. A summary of the XANES and EXAFS results at the Mo K-edge can be found in Table 4.5. For comparison, the edge energies for Mo foil, MoO₂ and MoO₃ are 3.2044×10^{-15} , 3.2063×10^{-15} , and 3.2069×10^{-15} J respectively.

Table 4.5: Summary of Mo K-edge XANES and EXAFS results from R-space fitting. Fitting range; κ^2 : $\Delta\kappa = 0.30$ - 1.07 nm^{-1} ; $\Delta R = 0.140$ - 0.310 nm . CN = coordination number; R = bond distance; $\Delta\sigma^2$ = mean-square disorder in the distribution of interatomic distances; ΔE_0 = energy offset. Samples were pre-treated in flowing H₂ at 723 K and measured in H₂ at RT. The estimated errors are: CN, ± 1 and R, $\pm 0.002 \text{ nm}$, within those typical for EXAFS fitting [221].

Sample	Edge energy (J $\times 10^{-15}$)	Scattering path	CN	R (nm)	$\Delta\sigma^2$ (nm ²)	ΔE_0
Na ₂ MoO ₃ ·2H ₂ O	3.20692	Mo-O	4	0.177	N/A	N/A
Pt ₁₀ Mo ₁ /Al ₂ O ₃	3.20464	Mo-O	0.9	0.210	0.00001	9.5
		Mo-Pt	4.7	0.272	0.00003	2.1
Pt ₁ Mo ₁ /Al ₂ O ₃	3.20483	Mo-O	1.5	0.206	0.00001	3.6
		Mo-Pt	1.3	0.273	0.00003	0.2

Mo-O bonds were observed in the bimetallic samples, indicating some of the Mo present is oxidized. The poorly defined feature at 3.2053×10^{-15} J in both PtMo catalysts suggest there is Mo⁺⁶ in the catalysts. A linear combination fitting of the Mo K-edge XANES conducted with the Demeter suite of software [226] using metallic Mo, MoO₂, and MoO₃ reference compounds show that both catalysts are best fit by a combination of metallic Mo and MoO₃. However, because of the large uncertainty in the fitting results, it was not possible to quantify the relative concentrations (percentages) of each oxidation state with the data. From the edge position, we can infer that the metallic Mo fraction is higher in the Pt₁₀Mo₁/Al₂O₃ sample than the Pt₁Mo₁/Al₂O₃ sample. This qualitative conclusion of higher metallic Mo fraction is consistent with the EXAFS finding of larger Mo-Pt correlation in the Pt₁₀Mo₁/Al₂O₃ sample, where each Mo had 4.7 Pt neighbors (compared to 1.3 in the Pt₁Mo₁/Al₂O₃ sample). As the Mo content increased, the fraction of Mo in MoO₃ increased. However, considering the much larger (10x) number of total Mo atoms in Pt₁Mo₁/Al₂O₃, the total number of metallic Mo sites was higher in this catalyst as well.

In summary, the XAS results are consistent with Mo existing in both metallic and Mo⁺⁶ oxidation states. These results are consistent with the presence of two types of Mo on the Al₂O₃ surface: Mo-Pt bimetallic nanoparticles and MoO₃ clusters. This interpretation of the XAS data

is consistent with a previous study of a carbon supported PtMo catalyst used for aqueous phase glycerol reforming [227]. The lack of Mo-Mo correlation indicates Mo was not segregated or forming the core of the bimetallic particles; rather, it was dispersed in the Pt-rich particles, hypothetically contributing as an oxophilic metal site surrounded by Pt. Existing phase diagrams for PtMo systems show formation of a single-phase alloy at very high temperatures (1073-2273 K) [225], while below 1073 K a thermodynamic alloy does not exist [228]. The catalysts used in this study were not annealed above 723 K. The absence of such bulk alloys at low temperatures suggests relatively unfavorable interactions between Pt and Mo. Despite this, the results of our characterization work suggest the two metals are in close enough contact to have a synergistic effect. While this interaction may cause electronic effects on the Pt, our DFT results indicate that it is most likely the proximity of these two distinct sites that results in the altered reaction pathway. The d- band effects on the Pt sites that may cause the aromatic ring to bind less strongly still do not explain the promotion of a tautomerization pathway; other studies have suggested distinct sites are responsible for tautomerization [30].

4.4 Discussion

m-Cresol deoxygenation on Pt has been previously studied on supported catalysts, with products and proposed mechanisms depending on the support material and reaction conditions [30, 31, 52, 72, 187, 229, 230]. Over metals such as Pt with a high affinity for hydrogenation, it is generally accepted that under HDO conditions, the aromatic ring must be saturated before C-O scission can occur [31, 32]. A study of phenol deoxygenation over Pt/Al₂O₃, at hydrogen pressure (0.3 MPa total, 3:1 H₂:phenol) comparable to the present study, reported production of primarily cyclohexanone and cyclohexanol [43]. Previous calculations and microkinetic modeling of guaiacol deoxygenation over the Pt(111) surface by Lu et al. [211] indicated that direct deoxygenation without initial ring hydrogenation is unfavorable. They concluded that reaction of catechol and phenol over the Pt catalysts must occur at corner, edge, or step sites over the Pt(111) surface. Other previous studies have also concluded that deoxygenation over noble metal catalysts may occur at

step sites [77]. Our results on Pt/Al₂O₃ and Pt/C support the idea of bifunctional catalysis, with hydrogenation occurring on Pt and deoxygenation on the support. The small amounts of deoxygenation products observed on Pt/C may be due to reaction on undercoordinated Pt sites.

The primary focus of this work is to elucidate the mechanism by which Mo can improve the deoxygenation activity and selectivity of supported Pt catalysts. Characterization results indicate a complex structure for the catalyst: in particular, both reduced Mo (present as a bimetallic with Pt) and oxidized Mo were observed to be present on the surface after in situ reduction. Either or both of these components may contribute to the observation of improved deoxygenation rates in Fig. 4.3 and Fig. 4.4. One possibility is that MoO_x species add additional Brønsted acid sites [231–233]. Previous studies indicate that oxidized modifiers like Mo and Re may introduce a possible route for dehydration [96]. In this study, the results in Table 4.2 demonstrate that addition of Mo did not affect the rate of 3-methylcyclohexanol dehydration, such that essentially all the dehydration activity could be attributed to the Al₂O₃ support. Therefore, it is unlikely that the deoxygenation observed in Fig. 4.4 for the PtMo/C catalyst results from Brønsted acid sites on MoO_x that function in analogy to the support but instead is the result of an additional pathway over the bimetallic surface. The differing trends in selectivity as a function of conversion also support this idea. However, some role for MoO_x species in promoting deoxygenation cannot be ruled out, and we note that chemistry over MoO_x-containing surfaces was not considered with DFT models in this study.

The DFT calculations reported above support the hypothesis that PtMo bimetallic surfaces can provide an additional route to deoxygenation. The oxophilicity of Mo may suggest a scheme in which Mo directly extracts an O atom, but here we report the effect appears to be more complex. First, Mo favors geometries of aromatic surface species with a more upright orientation through favorable Mo-O interactions at the surface (Fig. 4.6 and Fig. 4.7). This upright orientation is associated with lower barriers for the H transfer reactions required for tautomerization. The barrier to the subsequent C-O scission reaction is also reduced, which in this case can be attributed to the oxophilicity of Mo, which stabilizes adsorbed OH in the final state. The Mo in the bimetallic surface

does not necessarily supply a site that is widely active for deoxygenation, regardless of the reactant: calculation of 3-methylcyclohexanol deoxygenation over the PtMo surface was endothermic by 1.36×10^{-19} J, supporting the hypothesis that direct C-O scission of the alcohol is unlikely, even on the bimetallic catalyst surface. Similar observations of direct deoxygenation have been seen recently on SiO_2 supported materials. On Pt/ SiO_2 , the primary product formed was 3-methylcyclohexanone, resulting from a hydrogenation pathway; meanwhile, over a more oxophilic Ru/ SiO_2 catalyst, HDO became more prevalent [49]. We note that the highest energy barrier to tautomerization on the PtMo surface was calculated to be similar to the barrier for hydrogenation on the Pt surface (Fig. 4.6), consistent with the overall similar conversion rates of cresol (but with very different selectivities) observed experimentally for the two catalysts.

Thus, the results presented here suggest that use of noble metal - oxophilic metal combinations can influence selectivity in reactions of oxygenates in unexpected ways. That is, the strong interaction between Mo and the oxygenated functional group can stabilize adsorbate geometries that favor elementary steps that involve C-OH dissociation. An orientation effect altering the barrier for tautomerization has been observed previously for differences in phenol interactions between Pt and Pd at low hydrogen pressures [210]. Calculations by Nie et al. [32] for NiFe catalysts demonstrated that the Fe component strengthened interaction of alcohol functional groups with the surface, changing the adsorbate configuration; this observation was connected with increased deoxygenation selectivity on Fe- containing catalysts.

A previous examination of tautomerization over Fe(110) was performed by Hensley et al. [191]. This work found barriers of 3.25×10^{-19} and 3.89×10^{-19} J depending on orientation relative to the surface, indicating that tautomerization was not a likely pathway. In both reactions, the tautomerization did not include intra- molecular hydrogen transfer to the surface. Yoon et al. [234] also explored the tautomerization mechanism with barriers comparable to those of Hensley et al. [191] for reactions in ultrahigh vacuum conditions. Work by Tan et al. [49] showed that tautomerization may occur over the bare Pt(111) surface, though the barrier for subsequent deoxygenation is higher in this mechanism than if surface hydrogen is included. Thus,

the participation of the surface in tautomerization and the inclusion of hydrogen are both important to understanding the mechanism of deoxygenation.

4.5 Conclusions

Addition of Mo to supported Pt catalysts increased selectivity to deoxygenated products by creating sites that introduce a new preferred reaction pathway by changing the kinetic barriers. m-Cresol was proposed to follow a ring hydrogenation pathway over Pt but a tautomerization-deoxygenation pathway over PtMo catalysts, due to oxophilic sites that increase the interaction of the surface with oxygen-containing functional groups. DFT calculations suggested a bifunctional PtMo surface, which contains sites for hydrogen activation and sites for facile tautomerization of m-cresol, creates a lower energy barrier for deoxygenation. This lowered barrier may render deoxygenation reactions on the metal surface kinetically relevant, whereas a lack of bifunctionality (Pt) requires a separate acid function (from the catalyst support) for C-O bond cleavage.

Chapter 5

Use of computational models to predict an improved HDO catalyst

Previous work indicates that an optimal hydrodeoxygenation (HDO) catalyst may be a material with sites that bind O strongly and C weakly. In this chapter we model adsorption energy differences and use this information to predict an improved HDO catalyst by finding bimetallic surfaces that have a greater difference in C and O binding strengths than PtMo. CH₃ and OH were placed on the top site of various host and modifier sites respectively. Density functional theory calculations of the resulting adsorption energies with existing models for CH₃ and OH adsorption energy prediction. These results suggest that electronic properties such as the d-band center of the modifier site are important descriptors of the adsorption energy difference. Based on these calculations, PtW was found to have a larger gap in adsorption energies than PtMo. Preliminary experimental results suggest that PtW does have greater m-cresol deoxygenation activity than PtMo does. To further probe this model, PdFe (which computational results indicate should perform well for HDO) and PdMo (which should not have high HDO activity based on this model) were also synthesized and tested. The results agree with computational predictions, with PdFe more active than PdMo for m-cresol HDO.

5.1 Introduction

The results of the previous chapters suggest that an important factor in determining whether a catalyst will be selective for deoxygenation is how strongly it binds carbon and oxygen. Repulsion of aromatic rings, resulting in weakened binding to the surface, led to less decomposition (Chapter

3). In addition, increased interaction between the surface and oxygen-containing functional groups resulted in stronger binding through the oxygen group, effectively “pulling” the oxygen towards the surface and by doing so altering adsorption orientation to favor deoxygenation reactions (Chapter 4). Fig. 5.1 shows this proposed adsorption orientation with m-cresol as an example of an oxygenated reactant.

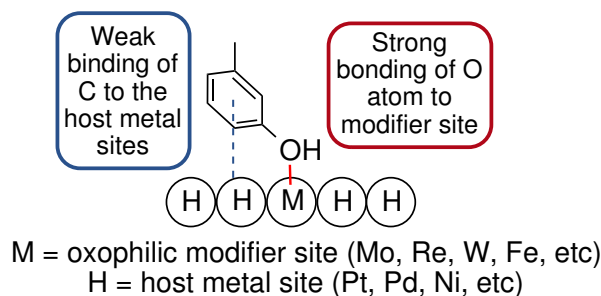


Figure 5.1: Proposed binding configuration for increased C-O scission of oxygenated reactants on bimetallic catalyst. M represents oxophilic modifier sites and H represents the host metal. The O group of the reactant (shown here as m-cresol) is strongly tethered to the surface at the modifier and the carbon ring is more weakly bound to the host metal sites.

Therefore, it may be possible to design an improved m-cresol HDO catalyst by tuning a bimetallic surface to have a larger difference in carbon and oxygen adsorption strengths. This can be probed using density functional theory (DFT) to calculate the adsorption energy of methyl and hydroxyl groups as a measure of binding an aromatic carbon ring and an oxygen containing functional group of a biomass-derived compound. This chapter contains modeling and experimental results as proof-of-concept work to demonstrate the potential for utilizing these trends in adsorption strength to design an improved deoxygenation catalyst. Further work is needed to gain a full understanding of the proposed model and how it applies to experimental results. These studies are currently in progress.

Previous work has shown that scaling relations can be used to calculate the adsorption energy of a desired reactant based on a known adsorption energy for a simpler molecule [235]. For example, CH_3 adsorption can be used to predict the adsorption energy of any alkyl [236]. This is true for

unsaturated compounds as well; the adsorption energy of ethylene vs carbon scales linearly for most transition metals, as shown in Fig. 5.2 [237]. This trend applies as long as sigma bonds are formed, i.e. for the metals to the left of Cu, Ag, and Au on the periodic table. We can therefore expect that the changes in adsorption energy of CH_3 on different surfaces will be proportional to the adsorption energy of the larger aromatic ring present in most reactants of interest to biomass upgrading. Similarly, OH adsorption should capture the trend in adsorption of oxygen-containing functional groups, such as alcohols, ethers, and carbonyls.

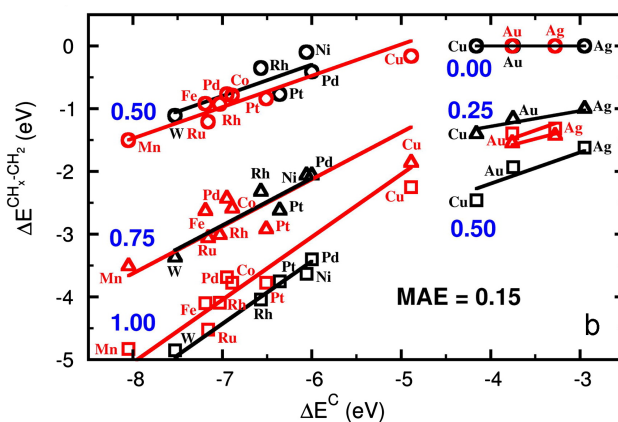


Figure 5.2: Adsorption energies of $\text{CH}_x\text{-CH}_2$ ($x=0, 1$, and 2) intermediates plotted against the adsorption energies of carbon (squares: $x=0$; triangles: $x=1$; circles: $x=2$). The adsorption energy of molecule A is defined as the total energy of A adsorbed in the lowest energy position on the surface minus the sum of the total energies of the isolated neutral species A and the clean surface. The data points represent results for close-packed (black) and stepped (red) surfaces of various transition metals. Reproduced from [237].

However, one issue that these scaling relation plots help to demonstrate is that a more reactive metal that binds oxygen more strongly typically binds carbon more strongly as well. This can be understood in terms of the d-band model, which says that the difference in adsorption energy of a given adsorbate on the same site of two different metals is primarily a function of the difference in the interaction between the adsorbate and the substrate d-states [238]. Since all transition and noble metals have a broad, partially filled s-band, the difference in adsorption energies has a very small dependence on these electrons [239]. Alternatively, the d-band electrons of these metals

are distinct for a given metal, and knowing the shape of their density of states (DOS) plot can be predictive of adsorbate binding. Sites on metals with a higher d-band center generally bind adsorbates more strongly than geometrically similar sites on metals with a lower d-band center. In general, moving right to left and upward on the periodic table results in increasing d-band center and therefore a more reactive metal. It should be noted that there are exceptions to this model, some of which are relevant to this work and will be discussed in more detail later.

One way to potentially break this trend in increasing adsorption strength of carbon along with oxygen is to use a bimetallic catalyst. By creating a bifunctional surface containing sites that bind oxygen strongly and other sites that activate hydrogen and interact with the carbon-containing portion of the reactant, a catalyst may be tuned to optimize this difference in adsorption strengths. Therefore, to build upon the studies performed earlier in this thesis and attempt to rationally design an improved deoxygenation catalyst, a series of DFT calculations were performed on various bimetallic surfaces to predict compositions that would yield high deoxygenation activity.

5.2 Methods

5.2.1 Computational methods

The Vienna Ab Initio Simulation Package (VASP) [149, 150] was used to perform density functional theory (DFT) calculations. The plane-wave basis set was cut off at 6.34×10^{-17} J and the projector-augmented wave method was used for the core electrons [120, 121]. The k-point mesh was $7 \times 7 \times 1$ for the geometric relaxations. Visualizations of these structures were generated using QuteMol [151].

DFT calculations were performed on various bimetallic surfaces that consisted of an FCC host metal with one modifier site created by substituting an atom of a dopant metal into the first layer. An example of the bimetallic surface structure is shown in Fig. 5.3. In separate calculations, CH_3 was placed on the top site of the host metal directly adjacent to the modifier site (Fig. 5.3a) and OH was placed on the top site of the modifier (Fig. 5.3b). The adsorption energies and geometries

of these probe molecules were calculated on the relaxed, optimized surface with the bottom two layers held fixed at the optimized bulk distance. This approximates the adsorption of more complex reactants, such as m-cresol, with interaction of the oxygen-containing functional group through the modifier site and the aromatic ring through the host metal, as shown in Fig. 5.1.

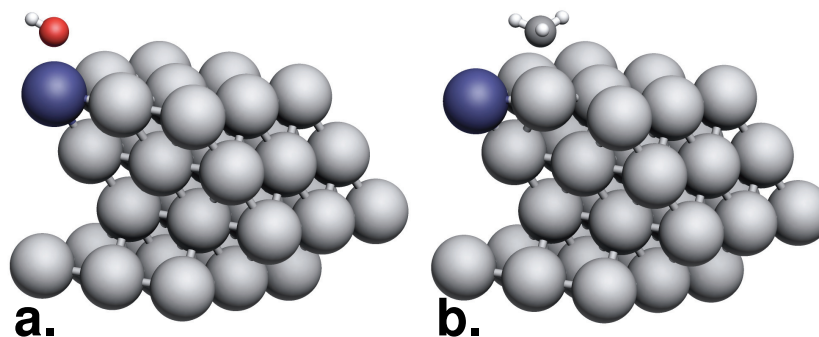


Figure 5.3: Example structure of a 111 slab of an FCC host metal with a modifier site substituted in. OH was placed on the top site of the modifier (a) and CH₃ was placed on the top site of the host metal (b).

5.2.2 Experimental methods

Supported catalysts were prepared by incipient wetness impregnation of a porous γ -Al₂O₃ support (Albemarle MARTOXID AN/I, 150 m²/g BET surface area, 75- μ m particle diameters) or carbon black powdered support (Vulcan XC 72R). Aqueous solutions were prepared of the metal precursors using chloroplatinic acid hexahydrate (Strem Chemical Inc.), ammonium molybdate tetrahydrate (Strem Chemical Inc.), ammonium tungsten oxide hydrate (Alfa Aesar), and ammonium tetrachloropalladate(II) (Alfa Aesar). PtMo/Al₂O₃ and PtW/Al₂O₃ catalysts were prepared via co-impregnation of the two precursors with a 1:1 atomic ratio of Pt:M (M= Mo, W), containing the same amount of Pt (5 wt%) with M added to create the desired composition at increased total metal loading. The catalysts were dried in air at 373 K and then calcined for 2 h at 723 K in 50 sccm He and 30 sccm O₂. PdFe/C and PdMo/C were prepared at a total metal

loading of 10 wt% with 1:1 atomic ratio of Pd:modifier; carbon supports have been used previously for cresol upgrading on PdFe and therefore was chosen here to compare with literature trends [65]. After co-impregnation the carbon supported catalysts were dried in air at 393 K for 10 h.

Upgrading experiments were performed in an atmospheric pressure tubular packed bed flow reactor. Prior to reaction the catalyst was reduced in-situ at 723 K for 1.5 h in 30 sccm He and 30 sccm H₂. The reactor was then cooled to 598 K to perform upgrading experiments. Reactants were introduced by bubbling helium through the liquid compound that was immersed in a water bath at 318 K. The saturated He was then mixed with H₂ and diluent He before flowing over the catalyst bed. The reactor effluent was analyzed using an Agilent Technologies 7890A gas chromatograph with a 30 m $\times$ 0.320 mm Agilent HP-5 (5% phenyl)-methylpolysiloxane capillary column and flame ionization detector.

5.3 Results and discussion

The large combinatorial space for bimetallic catalyst formulations makes experimentally testing each possibility inefficient. It is desirable to screen potential combinations computationally to rationally design promising catalysts to test experimentally. Ideally, this may be accomplished using physical properties and simple correlations that do not rely on computationally expensive calculations; running simulations of m-cresol HDO on each surface of interest would also be inefficient. Previous work has suggested that the most important physical characteristics are the metals' electronegativity, atomic radius, and spatial extent of valence orbitals [238]. By knowing these physical properties it may be possible to predict the d-band structure and the adsorption energy difference between adsorbates such as CH₃ and OH. To support the following model, DFT calculations were also performed to determine these adsorption energies. The resulting values can be seen in Table 5.1. The difference in adsorption energies, $E_{\text{ads}}(\text{CH}_3) - E_{\text{ads}}(\text{OH})$, is defined as ΔE_{DFT} .

In terms of the d-band model, the d-band filling is related to the number of occupied d-orbitals; the width of this band is dependent upon the number of neighbors the atom being

Table 5.1: Adsorption energy (E_{ads}) of CH_3 on a host metal site and OH on a modifier site from DFT calculations and the difference in these adsorption energies (ΔE_{DFT}) (all in J)

Host Metal	Modifier	$E_{\text{ads}}(\text{CH}_3)$ ($\text{J} \times 10^{-19}$)	$E_{\text{ads}}(\text{OH})$ ($\text{J} \times 10^{-19}$)	ΔE_{DFT} (J) $\times 10^{-19}$)
Pt	none	-4.18	-4.1	-0.1
Pt	Fe	-4.25	-5.22	0.98
Pt	Re	-4.25	-6.22	1.99
Pt	Mo	-4.09	-6.2	2.11
Pt	W	-4.21	-6.7	2.47
Pt	Ti	-4.17	-6.18	2.02
Pt	Co	-4.25	-4.95	0.7
Pt	Cr	-4.25	-5.93	1.68
Pt	Ni	-4.25	-4.63	0.38
Ag	none	-2.45	-4.6	2.15
Ag	Mo	-4.73	-7.53	2.8
Ag	Re	-4.84	-7.21	2.37
Ag	Fe	-4.18	-6.41	2.23
Ag	W	-5.16	-8.19	3.01
Ag	Ti	-4.6	-8.19	3.57
Ag	Co	-3.97	-5.88	1.91
Ag	Cr	-4.53	-7.48	2.95
Ni	none	-4.31	-5.7	1.39
Ni	Mo	-4.42	-6.28	1.87
Ni	Re	-4.28	-6.01	1.73
Ni	Fe	-4.58	-5.99	1.41
Pd	none	-3.8	-4.47	0.67
Pd	Mo	-4.17	-5.82	1.63
Pd	Re	-4.36	-6.49	2.13
Pd	Fe	-3.93	-6.46	2.53
Cu	none	-3.32	-5.48	2.16
Cu	Mo	-4.41	-7.37	2.96
Cu	Re	-4.6	-6.92	2.34
Cu	Fe	-4.26	-6.2	1.94

considered has to interact with as well as the spatial extent (or size) of the d-orbitals [238, 240]. When two metals are in close proximity so that they are interacting with each other, it is possible to change both the width and the filling of the d-band of either metal. Often the filling stays the same (there is no transfer of electrons from one metal to another) but the width of the band changes, therefore shifting the d-band center; for example, this is often the case for bimetallic combinations where the constituent metals have similar electronegativities [168]. The d-band width is proportional to the interatomic matrix element, which describes the bonding between the d-orbitals of a given atom and the d-orbitals of its neighbors [166]. This is a function of the bond

distance between neighboring atoms and the spatial extent of the d-orbitals, which is an intrinsic property of the given element [240].

Using these properties, one can predict the adsorption energy of adsorbates such as CH_3 by using previously developed relations [236]. When the local environment of a metal adsorption site is changed by introducing a second metal, not only does the d-band center change but the interaction between the adsorbate states and the altered metal d-states will change as well [238]. To predict the difference in adsorption energy between CH_3 and OH , Eq. (5.1) and Eq. (5.2) were used [241], where ϵ_d is the d-band center, ϵ_p is the p-band center, f is the d-band filling, V_{ad} is the interatomic matrix element describing interaction between the adsorbate states and the metal d-states, and β_i and γ_i are fitting parameters that were tabulated for these adsorbates in a previous study [241]. These parameters were obtained for the metal atom that the adsorbate was interacting with. For CH_3 this was the host metal and for OH it was the modifier. This was done by calculating the local density of states of the atoms in bimetallic surface. This allows the d-band and p-band centers for the modifier site and the host metal site adjacent to be computed. V_{ad} estimated using the relationship shown in Eq. (5.3), where r_d is the spatial extent (or size) of the d-orbitals in the given metal atom (tabulated previously [238]) and d is adsorbate-metal bond distance [236]. The actual values of V_{ad} were calculated by turning the proportionality in Eq. (5.3) into an equation using a constant. This constant is accounted for by normalizing all of the computed V_{ad} terms to one metal (in this case, $\text{Cu}(111)$ as has been done previously [241]). For simplicity, in the following discussion the adsorption energy difference between CH_3 and OH calculated using Eq. (5.1) and Eq. (5.2) will be referred to as ΔE_{model} .

$$E_{\text{ads}}(\text{CH}_3) = \beta_1 + \beta_2\epsilon_d + \beta_3\epsilon_p + \beta_4V_{ad}^2f \quad (5.1)$$

$$E_{\text{ads}}(\text{OH}) = \gamma_1 + \gamma_2\epsilon_d + \gamma_3\epsilon_p + \gamma_4V_{ad}^2f + \gamma_5V_{ad}^2 \quad (5.2)$$

$$V_{\text{ad}} \propto \frac{r_d^3}{d^7} \quad (5.3)$$

Fig. 5.4 shows ΔE_{DFT} , which uses the data in Table 5.1, plotted as a function of ΔE_{model} , which is calculated using Eq. (5.1) and Eq. (5.2). As shown by the resulting parity plot, this relation captures the trend in adsorption energy difference for a wide variety of bimetallic surfaces.

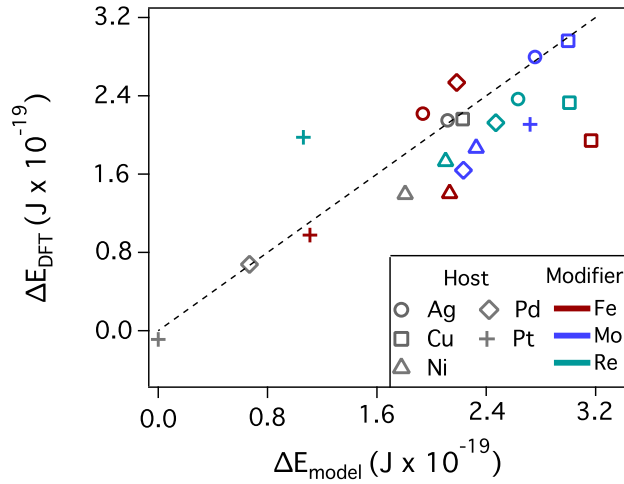


Figure 5.4: Difference in DFT-calculated adsorption energy of CH_3 vs OH on the top site of various bimetallic surfaces (ΔE_{DFT}) as a function of the difference in the model-calculated adsorption energies (ΔE_{model}) as shown in Eq. (5.1) and Eq. (5.2). OH was located on the top site of the modifier and CH_3 on the top site of the host metal (in separate calculations, see images in Fig. 5.3).

These adsorption energy differences calculated with DFT are also shown in Fig. 5.5 to more easily compare each bimetallic combination, including a wider variety of modifier sites. The first category shows the energy difference for the pure host metal (differentiated by color as shown in the legend) and the following show the difference between CH_3 on that host metal and OH on the given modifier site.

As Eq. (5.1), Eq. (5.2), and Eq. (5.3) suggest, there are many physical and electronic properties influencing adsorption strength. One objective of this work is to understand how the underlying electronic properties of these bimetallic surfaces correlate with the difference in C and O adsorption strengths. The models in Eq. (5.1) and Eq. (5.2) worked well for a variety of surfaces,

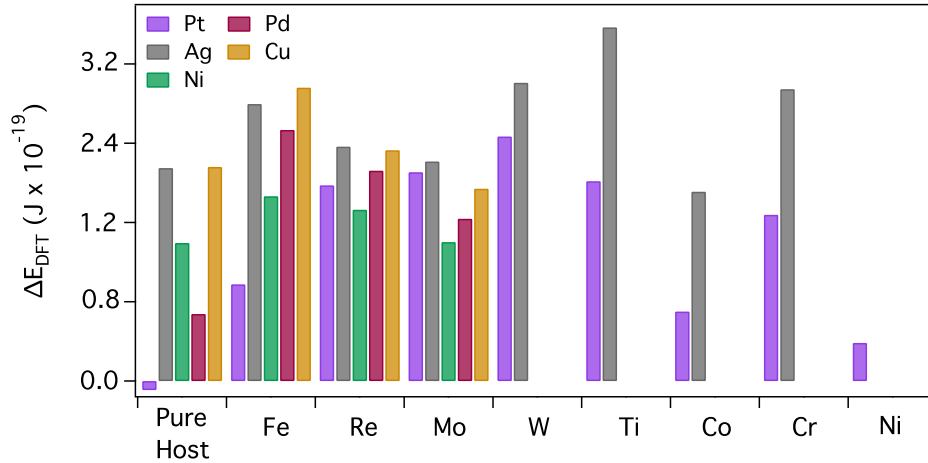


Figure 5.5: Difference in adsorption energies of CH_3 vs OH for each surface modeled. The host metal is shown by the color in the legend and the modifier identity is shown by the category on the x-axis. From left to right in each category these are Pt, Ag, Ni, Pd, and Cu (111) surfaces.

indicated by the good agreement between the model and DFT in the parity plot in Fig. 5.4. The results reported here suggest that there is a correlation between the electronic structure of the two metals and the binding energy difference. One potential issue with this model is the amount of scatter in Fig. 5.4. The study that developed Eq. (5.1) and Eq. (5.2) had a much tighter fit around the $y=x$ line. The likely cause of increased scatter in this work is that the fitting parameters (β_i and γ_i) were primarily based on homogeneous surfaces [236]. The surfaces used here, with a modifier site surrounded by host atoms of a different metal, are very different; it is therefore likely that using Eq. (5.2) for an atom that is surrounded by another element may be in error.

One cause for the larger differences in CH_3 vs OH adsorption energies for some bimetallic combinations over others may be the resulting d-band center of the modifier site. The calculated d-band center of the modifier sites varied based on the host metal they were inserted into, but the host metal sites did not have as significant of a d-band shift after modifier incorporation. The calculated d-band center for the modifier sites varied less than 2.40×10^{-20} J from the unmodified surface; the average deviation over the surfaces shown in Fig. 5.4 was 8.01×10^{-21} J. However, the d-band center of the modifier sites was much more dependent on its neighboring atoms, varying by as much

as 1.60×10^{-19} J. This seems to correlate with the observed differences in adsorption energies after incorporating a modifier site. As shown in Table 5.1, while the CH_3 adsorption energy did not change drastically based on the modifier site present, the OH adsorption energy did. The majority of the difference in ΔE_{DFT} comes from changing $E_{\text{ads}}(\text{OH})$. For example, when comparing PdMo to PdFe, the 8.81×10^{-20} J difference in adsorption energies has 2.40×10^{-20} J contribution from CH_3 adsorption and 6.41×10^{-20} J from the adsorption of OH on the modifier site. Therefore, a simplified explanation for one major cause of the increased bias between these adsorption strengths may be the electronic structure of the modifier site in the given host metal. Thus, in order to use Eq. (5.2) to more accurately predict adsorption strength and mitigate some of the issues with scatter discussed above, a new model likely would need to be developed. By fitting the model on DFT calculations of these bimetallic surfaces more accurate parameters may be developed. Instead, for this preliminary work we have focused on identifying surfaces combinations of metals that have large adsorption energy differences and understanding why these large differences may be present.

Additionally, it may be informative to consider these differences in adsorption energy relative to the pure metal. Each host metal has some inherent difference in how strongly it binds OH and CH_3 . However, these monometallic catalysts do not make the best deoxygenation materials. Some metals, for example Ag, have large relative differences (see Fig. 5.5) despite the fact that they bind both CH_3 and OH weakly and have other undesirable properties such as low activity for hydrogen activation. By subtracting this monometallic case out it may be easier to distinguish bimetallic combinations in which the modifier site is having a significant contribution to the adsorption energy difference. Fig. 5.6 shows these relative differences in adsorption energy. When the contribution of the pure host metal is subtracted out it is clear that Pt based combinations show the largest adsorption energy differences of all metals screened. It is also important to note that Pt is an excellent catalyst for H_2 activation and hydrogenation, key elementary steps in the overall HDO reaction.

Based on Fig. 5.5 and Fig. 5.6, PtMo is expected to be a good bimetallic combination but PtW appears even more promising. In addition, these figures show a large difference in adsorption

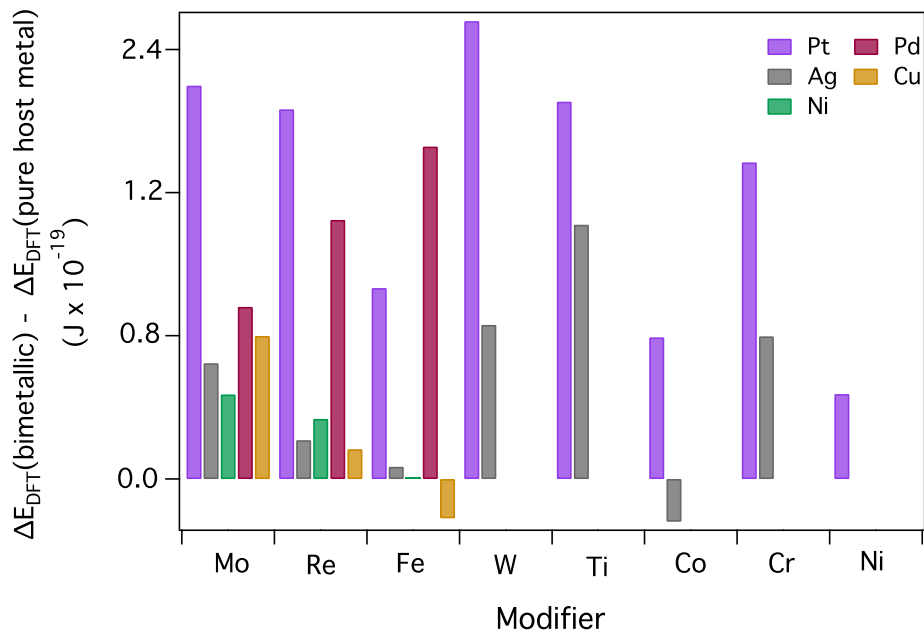


Figure 5.6: ΔE_{DFT} in J relative to the pure metal surface plotted for each host metal as a function of modifier site.

energies over PdFe, which has previously been shown to be active for HDO [50, 65] but not over PdMo. To test the predictions of these calculations for HDO performance, supported PtW, PdFe, and PdMo catalysts were prepared and tested for m-cresol HDO. For comparison with previous work done in this thesis using PtMo, a $\text{Pt}_1\text{W}_1/\text{Al}_2\text{O}_3$ catalyst was made using the same incipient wetness coimpregnation technique used for PtMo. To compare with previous literature using PdFe catalysts, $\text{Pd}_1\text{Fe}_1/\text{C}$ and $\text{Pd}_1\text{Mo}_1/\text{C}$ were also synthesized using incipient wetness impregnation. The initial rates for m-cresol HDO at atmospheric pressure and 598 K are shown in Fig. 5.7. The only product formed under these conditions was toluene. Previous studies of HDO on PdFe has shown aromatic production as well [50, 65].

5.4 Conclusions

Two key factors that indicate a catalyst will be active for HDO are strong binding of oxygen and weak binding of carbon. This can be accomplished using bimetallic catalysts containing a host

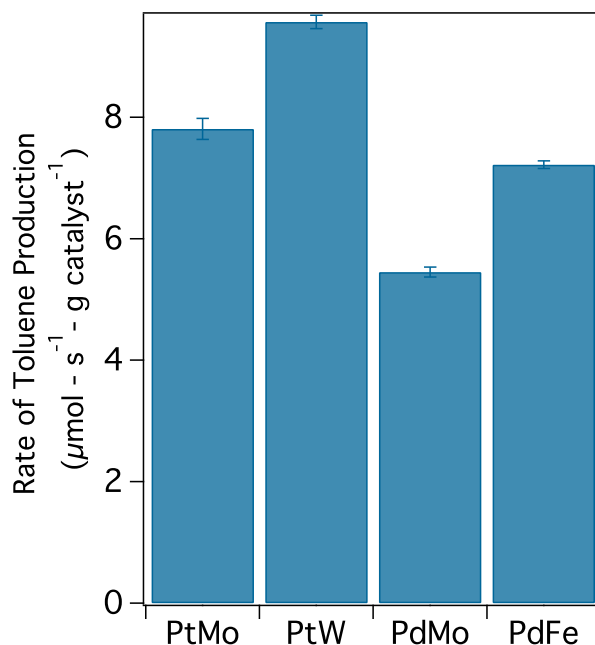


Figure 5.7: Rate of product formation for m-cresol HDO over Pt and Pd based bimetallic catalysts. Reactions were carried out at atmospheric pressure and 598 K with the same ratio of hydrogen:cresol over each catalyst. Conversions were $<3\%$.

metal that activates hydrogen and interacts with the carbon-containing portion of the reactant and a modifier site that strongly interacts with the oxygen functionality. As proposed previously in literature, by tuning electronic properties of the two metals the adsorption energies of C and O can be tuned as well. An analysis of the binding energy difference between CH_3 and OH suggests that PtW catalysts may be more active for deoxygenation than PtMo, and that PdFe may be more active than PdMo. Preliminary experimental results for m-cresol HDO agree with this expected trend, with PtW and PdFe having higher initial rates for HDO than PtMo and PdMo.

Chapter 6

Conclusions

In summary, the addition of an oxophilic metal, such as Mo, to noble metal catalysts, improves deoxygenation selectivity for reactants including benzyl alcohol and m-cresol. When Mo is oxidized it has no promoting effect and merely blocks active sites. However, after partial reduction Mo interacts with neighboring Pt atoms and has a significant electronic effect, as evidenced by X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) experiments.

An important question about these materials is the structure of the catalyst under reaction conditions. Characterization of the Mo/Pt(111) model surface by XPS showed that reduced Mo prefers to reside in the subsurface layers, which is in agreement with previous computational studies. Density functional theory (DFT) calculations showed that subsurface Mo serves to reduce the adsorption strength of reactants, especially aromatic compounds. This was true of adsorbates bound by carbon, shown by adsorption of toluene, and those bound through oxygen, shown by benzyl alcohol calculations. Experimental results support this as well; for example, CO TPD showed decreasing desorption temperature as Mo coverage increased and complete decomposition of benzyl alcohol was suppressed after incorporation of Mo. While migration into the subsurface likely occurs on supported catalysts, X-ray absorption spectroscopy results indicate that a portion of the Mo also resides on the surface of the nanoparticles. In this case, the more reactive Mo sites bind adsorbates, particularly oxygen, more strongly. DFT calculations using m-cresol adsorbed on a surface Mo site in Pt(111) showed that this increased adsorption strength may serve to alter the reactant's orientation and facilitate tautomerization.

Mo incorporation in the subsurface (to weaken adsorption, especially of carbon) or surface layer (to strengthen adsorption, especially of oxygen) has been used to hypothesize the cause of increased HDO activity over PtMo catalysts. For example, subsurface Mo weakening metal-adsorbate interactions was proposed to suppress benzyl alcohol and toluene decomposition. It is possible that subsurface Mo leads to weakened adsorption energy of benzyl alcohol by altering the adsorption orientation, thus increasing deoxygenation activity. The high deoxygenation activity of benzyl alcohol over small Pt particles is evidence of this; the defect sites may alter adsorption orientation even in the absence of Mo. Alternatively, surface Mo atoms on supported catalysts were proposed to increase the metal-oxygen interaction, facilitating m-cresol tautomerization. M-cresol tautomerization was not facilitated even over small Pt particles with a large fraction of defect sites, indicating that for this reaction the promotion effect of Mo may be different than for benzyl alcohol. Instead of influencing adsorption orientation through subsurface Mo weakening the interaction, surface Mo atoms that could strongly tether the oxygen-containing functional group may be critical. With this in mind, future work should focus to better understand the surface structure of the bimetallic catalyst under reaction conditions. For instance, while there is support for the hypothesis that the majority of Mo is subsurface on Mo/Pt(111), it is not clear if the active surface under reaction conditions does have a significantly higher population of surface Mo atoms. Characterizing this structure may be important to thoroughly understanding catalyst performance. Using in-situ spectroscopy with high enough resolution to identify the location of the Mo atoms in the bimetallic surface as well as the approximate cluster size of these Mo sites will allow more accurate DFT models to be created. While the models employed in this thesis have provided useful information to support experimental results, their accuracy depends on an informed prediction of the surface structure. Further probing the structure of the bimetallic surface and using computational approaches for this updated model of a PtMo catalyst under reaction conditions may provide additional insight into the deoxygenation mechanisms that have been proposed in this thesis. It may also further advance the application of models like those used in the final chapter of this thesis to better predict an optimal deoxygenation catalyst for the HDO reaction of interest.

The results of this work demonstrate the importance of collaboration between surface science, supported catalyst research, and computational efforts. Combining these techniques and using the results of one approach to inform hypotheses and experiments using the other two, provides a much more fundamental understanding than would be possible by relying on one alone. Ultimately this deeper understanding of a promising material can be used to inform the design of the next, allowing the field to advance more quickly towards goals such as making large-scale biorefining a reality.

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