Bimetallic Catalyst for Lignin Depolymerization

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Bimetallic Catalyst for Lignin Depolymerization

By

Qishen Lyu

A thesis presented to the McKelvey School of Engineering of Washington University in St. Louis in partial fulfillment of the requirements for the degree of

Master of Science

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# Catalogue

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This thesis is motivated by concerns regarding the need to develop more sustainable and economic technologies to meet rising global manufacturing and energy demands. These concerns have renewed governmental, industrial, and societal determination to reduce the world’s dependence on conventional natural resources and has led to considerable research on producing fuels and chemicals from feedstocks other than petroleum. Lignocellulosic biomass represents an abundant and renewable resource that could displace petroleum feedstock producing biofuels and multiple valuable chemical products with reduced greenhouse gas emissions. Lignin is the second abundant biopolymer source in nature and is found almost everywhere. Since the 1950’s, there have been reports of lignin depolymerization research to develop valorization technologies that convert lignin in energy, fuels, and chemicals through thermal and biological approached. Most of these technologies targeting chemical production have insufficient processing and economic performance for widespread...
adoption, in part due to lack product selectivity that results from lignin depolymerization. Heterogeneous metal catalysis is an ideal solution for improving lignin depolymerization process performance by promoting more selective reactions under lower energy input. Among different kinds of catalytic systems, a copper-doped porous metal catalyst has been researched often due to the ability to product hydrogen via alcohol reforming and perform hydrogenolysis for lignin depolymerization at aryl-ether linkages. However, the use of nickel in other catalytic systems suggest a nickel-doped catalyst might have a greater ability hydrogenolysis on aryl-ether linkages, further reducing the lignin linkage activation energy and improving product selectivity. This thesis will focus on the development of a bimetallic catalyst with copper and nickel co-doped on a hydrotalcite support, testing the hypothesis that a bimetallic catalyst containing copper and nickel will have better reforming ability than a catalyst containing only nickel and will have better hydrogenolysis of aryl-ether ability than a catalyst containing only copper. Chapter I will present a detailed overview of the background and motivation of lignin structure and conversion. Chapter II will present detailed research on the performance of copper and nickel bimetallic catalysts for the hydrogenolysis of a lignin aryl-ether model compound. Chapter III will present unfinished work and future plan about using the catalysts been made in Chapter II for real lignin test.
Chapter I: Introduction

1.1 Overview

Fossil resources, particularly coal and oil, have been the major source of energy and carbon, and with rapid growth in industrialization and human population, the demand for energy and carbon will continue to increase. Unfortunately, this demand for fossil resources has been accompanied by serious environmental issues, such as global warming and air pollution. With the increasing utilization of fossil resources, it is estimated that greenhouse gas and other pollutants emission will increase by ~30% over the next 20 years,\(^1\) leading to increases in environmental and human health problems. In order to mitigate these concerns, research into renewable energy and carbon sources, such as biomass, has become much more prevalent.\(^2\) With the development of biorefining, biomass can be used as a source of energy and carbon producing renewable fuel, chemical, and material, while decreasing carbon emissions into the atmosphere.

A biorefinery involves “the sustainable processing of biomass into a spectrum of marketable products and energy”\(^3\). Unlike the carbon within fossil resources, biorefineries focus on using the energy and carbon stored inside plant tissues which captures solar energy and atmospheric carbon through photosynthesis on a time-scale making plants a renewable resource. First generation biorefineries use food crops to generate products like bio-alcohol or bio-diesel.\(^4\) Typically, first generation bio-products require plant-derived starches, sugars, or oils, and have been used widely for
decades with some successful products even being cost competitive at times with traditional fossil fuels. However, choosing food crops as biofuel feedstock bring some significant disadvantages such as indirect land use changes, competing with food crops, soil erosion, biodiversity loss, chemical fertilizer pollution, and other environmental impacts. These issues have greatly limited the large-scale development of first generation biomass energy.

However, second generation biorefineries focus on using lignocellulosic biomass to make fuel, chemical, and material products. Lignocellulosic biomass are plants composed of cellulose, hemicellulose and lignin, and include a wide array of grassy and woody energy crops, wood product waste, and agricultural waste. The abundance of lignocellulose makes it a potential route for economic development for agricultural industries and rural areas. For now, second generation bioproducts are primarily produced from plant-derived carbohydrates (e.g., cellulose and hemicellulose), while generating large amounts of lignin as waste. As a result, and along with paper pulping waste lignin, lignin is an abundant but under-utilized resource. This fact along with the aromatic sub-structure of lignin makes lignin an ideal platform for valuable aromatic chemical production. However, the complex and recalcitrant structure of lignin makes it difficult to depolymerize lignin at mild reaction condition or into a narrow distribution of compounds amenable to product separation. Thus, there are no large-scale lignin conversion processes for chemical production.
1.2 Motivation

As a part of lignocellulose biomass, lignin is the second most abundant terrestrial biopolymer. About 300 billion tons of lignin are produced through photosynthesis globally. Industrially, 100 million tons of lignin with the value of 732.7 million dollars has been produced worldwide in 2015, and with the annual growth rate of 2.2%. Among the lignin production industry, 88% of waste lignin production is in the form of lignosulphonate while 9% of lignin production is Kraft lignin both of which are important by-products in papermaking and pulping. Only about 2% of lignin production is organosolv lignin with the increasing production due to the demand for biofuels. Nevertheless, most lignin is viewed only as waste. For example in bio-ethanol production, residual lignin either extracted before enzymatic hydrolysis to increase sugar yield or found in the post-fermentation solids is used as a fuel for local process heat and electricity production. Only ~2% of waste lignin produced is been sold for integration into products such as dispersants, adhesives, and surfactants. The amount of lignin waste will only increase, assuming there will be a demand for plant-derived carbohydrates for fermentative biofuel and biochemical production. Considering the economic and carbon cost associated with lignocellulosic biomass planting, agronomic input, and transport, utilization of lignin for local process heat and electricity production is insufficient to make biorefineries have a positive economic and environmental impact.

Although lignin conversion research has been a focal point for decades, the commercial implementation of a large-scale lignin conversion has yet to be achieved. Lignin is highly resistant to deconstruction, and thus, very challenging to selectively
depolymerize into its constituent aromatic monomers. This problem is further complicated by the diversity in lignin structures from different plant sources and the propensity of its depolymerization intermediates towards secondary reactions. Pyrolysis, a common non-catalytic thermochemical biomass conversion approach, generates an organic liquid from lignin. However, this liquid product has such a wide distribution of compounds that isolation or downstream processing of any particular compound for chemical production is impractical. Accordingly, stabilized and deoxygenated lignin pyrolysis products have potential utility only as precursors to liquid transportation fuels.

Fortunately, the monomeric structure of lignin makes it an ideal feedstock for renewable aromatic chemical production. Aromatic compounds only make up about 1% of compounds in crude oil but have a tremendous value in solvent, chemical and material production and markets. Petroleum-derived aromatics are converted into a wide-array of commodity and specialty chemical compounds, having several times the value per carbon that than carbon in petroleum-derived fuel. Because of the petrochemical and aromatic fractions separated from crude oil, the economics of oil recovery and refining are not solely related to and justified by fuel prices but rather is linked to and supported by the demand and profits from a wide range of diverse and profitable markets and downstream products. Similarly, the conversion of lignin into aromatics and phenolics is the type of product diversification necessary in a biorefinery to minimize the risk associated with “front-end” operations and to mitigate fluctuations in commodity fuel markets. Also, when considering of the environmental impact of
petroleum-derived phenol production, more than 98% of current petrochemical phenol manufacturing capacity (9.9 M tons) involves the cumene-hydroperoxide process and leads to one of the highest greenhouse gas emissions in the conventional refinery (5.8 kg CO2-equiv. per kg phenol). A life cycle analysis estimate for poplar-derived phenol is much lower, at just 3.4 kg CO2-equiv. per kg phenol.\textsuperscript{14} Thus, the wide spread production of renewable aromatics and phenolics could have a significant on greenhouse gas emissions.

Therefore, my research is motivated by the development of technologies that produce renewable aromatic (i.e., benzenes, toluenes, xylenes, etc.) and oxidized aromatic (phenolics, benzoic acids, etc.) compounds from lignin depolymerization and conversion processes.\textsuperscript{10} Lignin was designed by nature to be a protective cell wall element and thus molecularly heterogenous and difficult to deconstruct. However, successful development of biorefineries will require routes to both valorize cell wall carbohydrate and lignin fractions. Hence, this thesis will explore a method to promote lignin depolymerization via hydrogenolysis that does not require an external source or hydrogen and that produces a narrow product distribution due to decreases in the activation energy of lignin linkage cleavage.
1.3 Lignin Overview

1.3.1 What is lignin

Lignin is the term for a class of polymer with aromatic monomers based on hydroxycinnamyl alcohols.\textsuperscript{15,16} In nature, lignin is one of three major biopolymer (i.e., cellulose, hemicellulose, and lignin) in lignocellulosic plant cell walls. Softwoods contain 25-35% lignin, hardwoods contain 18-25% of lignin, while grasses, such as wheat and corn straw, contain 17-18% lignin.\textsuperscript{11} The lignin structure and content will change within the different organs and tissues of a single plant, responding to multiple environment and development factors.\textsuperscript{14} In the plant cell wall, lignin usually located as part of an interlaced network with hemicellulose around cellulose fibrils. Lignin is responsible for the structural integrity of the plant xylem, supporting water transportation and plant growth.\textsuperscript{17} The properties of lignin such as hydrophobicity and random monomer and inter-monomer sequencing helps the plants resist deconstruction in nature by microbial enzymes or other environmental elements.\textsuperscript{18} This design to resist deconstruction, also makes industrial lignin depolymerization challenging.
1.3.2 Lignin structure

Lignin is structurally heterogeneous and lacks a defined monomer sequence or molecular structure. The phenolic groups monomer in lignin structure usually referred to as “monolignols”.\textsuperscript{19} Lignin is both topologically entangled and chemically cross-linked with cell wall carbohydrates.\textsuperscript{19, 20} Although more than 35 lignin monomers have been identified, there are three main lignin monomers found in most lignocellulose plants. The three major monolignol monomers of lignin are phenylpropanoids, all of which are methoxylated to various degrees: \textit{p}-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol.\textsuperscript{21} After biosynthesis, these monomers are transported to the developing secondary cell wall and linked radically together through a series of oxidation and polymerization reactions initiated by enzymes (e.g. laccases, peroxidases, polyphenol

\textbf{Figure 1.1} A representation of lignin structure.
oxidases) to form a polymer similar to that shown in Figure 1.1, which is a representative lignin polymer.22

Lignin is polymerized in the cell wall with no biochemical control and thus no sequence control over monomer and inter-monomer linkages, forming lignin with different arrangement and proportions of sub-structures. This variation is observed from species to species and even from different parts of a single species.23 The process of monolignol transport into and polymerization within the cell wall is referred as lignification.15, 24 These monolignol monomers, once integrated in a lignin polymer, are known as p-hydroxyphenyl (S), guaiacyl (G), and syringyl (H) subunits.25 The distribution of G, S, and H monomers.26 Lignin from grass are more abundant in H, G, and S units while lignin from hardwoods is more abundant in G and S units and lignin from softwoods are abundant in G units.27 Lignin monomers are linked by several inter-monomer linkages and these linkages can be divided into two types: ether linked (C-O) and carbon-carbon linked (C-C) typical linkages.

There are four main aryl-ether linkages in lignin: aryl ether (β-O-4 and α-O-4), phenylcoumaran (β-5), and diaryl ether (4-O-5). Typical lignin C-C linkages include 5-5 linkages, β-1 linkages, β-5 linkages, and α-1 linkages (shown in Figure 1.2). The most common inter-monomer linkage is the β-O-4 linkage which comprise ~50 and 60% of the linkage in lignin from softwood and hardwood, respectively.27 β-O-4 linkages are therefore the most abundant linkage in most lignin. The abundance of β-O-4 and other aryl-ether linkages give rise to a pathway for lignin depolymerization process. Ether linkage as easier to break that carbon-carbon bond linkage and there provide weaker
elements in the lignin chain to target for cleavage. By developing chemistry to break ether linkages at relatively low temperatures, selective chain scission reactions can be promoted while preventing secondary reaction which cause product proliferation.

![Diagram of lignin monolignol monomers](image)

**Figure 1.2.** Three types of lignin monolignol monomers for lignin biosynthesis.

### 1.4 Current lignin conversion methods review

Lignin conversion methods can be mainly divided into three categories: thermochemical, biological, and hybrid conversion method. Thermochemical conversion methods focuses on using high temperatures and pressures to promote a reaction network that leads to lignin depolymerization and the generation of liquid and gas products. Depending on the conditions, a sub-set of reactions within this network can be selected leading to the more selective generation of desired products.

Lignin can be converted into a gas or liquid product via gasification and pyrolysis. Lignin gasification usually operated at the temperature higher than 900 K, transforming feedstock into carbon monoxide and other combustible gases with the addition of sub-
stoichiometric amounts of oxygen. Syngas, the gas product collected from gasification, has a wide array of applications such as a fuel or chemical precursor via Fischer-Tropsch processing. However, the high temperatures needed require significant energy input and push all the products towards a thermodynamically favored carbon monoxide intermediate. Although, carbon monoxide can be produced fairly selectivity, the deconstruction of biomass into carbon monoxide for upgrading and reconstruction of oxygenated hydrocarbons and aromatics waste the effort of photosynthesis to build biomass with useful molecular structures. Lignin pyrolysis is a method operating at a lower temperature than gasification and conducted in the absence of oxygen. Pyrolysis is an effective approach to depolymerization lignin; however, employs harsh reaction conditions for lignin depolymerization. Thus, non-catalytic pyrolysis generates an organic liquid with such a wide distribution of compounds that isolation or downstream processing of any particular compound is impractical.

Oxidation cracking of lignin, targeting lignin for the production of ketones, aromatic aldehydes, and carboxylic acids, involves relatively low temperatures (60-160 °C) but requires high pressures of oxygen and has low product yields. Traditional lignin oxidation methods including pulp bleaching with Cl₂ as oxidant; alkaline nitrobenzene oxidation (NBO) using nitrobenzene as oxidant under alkaline condition (NaOH) for lignin oxidation; and wet air oxidation (WAO) method, using oxygen or air in aqueous condition and a copper catalyst. One the other hand, reductive methods, including hydrogenolysis and solvolysis, depolymerize lignin by attacking C-C and C-O bonds via reaction with hydrogen gas. One of the key
advantages of hydrogenolysis is that it can operate alongside solvents, which can also facilitate solvolysis at the same time.

These thermochemical methods have drawbacks with respect to both yield or selectivity toward specific compounds, as a result introducing catalyst has proven as a very attractive. Thermal catalytic lignin depolymerization efforts focus on narrowing downstream product distributions, making product separation and purification more practicable, and affording more tractable chemical production. Research shows that aryl ether linkages such as β-O-4 and α-O-4 linkages are easy to break and are abundant in most lignin structures. A conversion route using catalyst to target selective cleavage of aryl ether linkages at mild conditions can achieve narrower product distribution by avoid secondary and side reactions. Both homogeneous and heterogeneous catalysts have been developed for thermal catalytic conversion of lignin. A homogeneous catalyst exists in the same phase as the substrate, usually in the liquid phase. Homogeneous catalysts have been developed for the selective hydrogenolysis of aryl-ether linkages, widely demonstrated on lignin model compounds with advantageous kinetics due to minimal transport limitations and well-defined active sites. However, such catalysts are likely to be too fragile and expensive for large-scale use, especially considering that quantitative recovery of the soluble catalyst from the products is likely to be difficult. As a result, heterogeneous catalysts, normally as a solid, can be used for reaction in liquid or gas phases as a more robust and more easily separated catalyst.
1.5 Metal catalysis of lignin

1.5.1 Single metal catalysts

Exploration of lignin’s reactivity towards H₂ dates back to the 1930s. In hydrogenolysis, H₂ causes reductive cleavage of C-X (X = O, S, Cl, or F) bonds. In contrast, hydrogenation saturates aromatic C-C bonds. The desired hydrogenolytic cleavage of aryl ether bonds, such as β-O-4 and α-O-4 linkages, is generally facile relative to other types of bonds found in lignin. Earlier studies with heterogeneous catalysts include reductive lignin depolymerization with hydrogen by noble metal catalysts on a variety of supports. Song et al. observed significantly different conversions of lignosulfonate to organic liquids and selectivity for the production of propyl guaiacol and 4-ethylguaiacol depending on the catalytic metal and support used. They evaluated 21 different catalysts including: RANEY®’s catalysts (Cu, Fe, and Co), precious metal catalysts (Pd/AC, Ru/AC, and Pt/AC, AC: activated carbon) and transition metal catalysts (Cu/AC and Ni/MCM-41). The aforementioned work not only illustrates how catalytic activity and selectivity for lignin depolymerization are greatly affected by the type of catalytic metal or support but also by lignin source, reaction temperature, and reaction solvent. Ye et al suggested the change in selectively as a result of the hydrogenolysis of lignin from corn stover versus that from bamboo was due to the differences in monomer distribution. Moreover, when alcohols were used as the solvent, significantly better hydrogenolysis activity was observed than when water was used due to hydrogen donating ability. In addition, the overall increases in lignin solvation and the rate of solvolysis observed when conducted at sub- versus
super-critical conditions, thus illustrates the sensitivity of lignin depolymerization kinetics to temperature.

An earlier report indicated that alkaline bases (e.g., KOH) facilitate the depolymerization of lignin and aryl-ether models in supercritical methanol (sc-MeOH). Further examination concluded that this occurred via base-catalyzed hydrogenolysis rather than hydrolysis of the C-O bond, and furthermore, that the reaction appeared stoichiometric in the base. These observations led Dr. Peter Ford at University of California Santa Barbara and coworkers to examine solid bases as recyclable and reusable alternatives to soluble bases. Porous metal oxides (PMOs) obtained by the calcination of synthesized Mg/Al 3:1 hydrotalcites (HTCs) exhibit characteristics of strong bases when doped with metal ions. For instance, the solid base Fe-PMO catalyzes the transesterification of triglycerides derived from seed oil to fatty acid methyl esters common in bio-diesel fuels. A series of transition metal ion doped PMOs were evaluated for their activity on the β-5 lignin model, 2,3-dihydrobenzofuran. Following these studies, catalytic hydrogen transfer from supercritical methanol (sc-MeOH) catalyzed by copper-doped porous metal oxide (CuPMO) was evaluated with lignin model compounds, organosolv lignin and even biomass such as sawdust. In fact it was determined that organosolv lignin depolymerizes over CuPMO in sc-MeOH, with the required H₂ for hydrogenolysis coming from reforming of the alcohol solvent and with minimal char formation. By triggering reforming reaction of the solvent, CuPMO catalytic hydrogenolysis does not require external sources of H₂ through the reaction shown in Eq.1.1 and Eq.1.2.
Unpublished work Susannah Scott at University of California Santa Barbara and coworkers, indicates that the growth of Cu nanoparticles on the surfaces of CuPMO occurs when exposed to sc-MeOH; however, there was no direct correlation made between the growth of such particles and the activities/selectivities of these catalysts. Specifically, x-ray spectroscopic data supports the formation of Cu(0) clusters over time; XANES spectra shows a shift to lower photon energy with longer use of the CuPMO which corresponds to Cu$^{2+}$ becoming progressively reduced to Cu(0) in sc-MeOH. Furthermore, the extended X-ray absorption fine structure (EXAFS) data indicates progressive decrease in Cu-O neighbors and increase in Cu-Cu neighbors implying formation of Cu(0) clusters. This data is corroborated by other preliminary data showing spherical shapes in the scanning electron microscope (SEM) image as well as Cu(0) diffraction peaks in X-ray powder diffraction (XRD) spectrum. In addition, variable temperature-flow reactor studies show that the calcined CuPMO catalyzes MeOH reforming as low as 230 °C,\textsuperscript{37} generating the H$_2$ needed to disrupt the lignin structure. In summary, once the catalyst has been activated: (1) exposed to a reducing environment, (2) Cu extruded from the metal oxide framework, and (3) Cu nano-clusters formed, it is capable of producing H$_2$ at even much lower temperatures.
1.5.2 Bimetallic catalyst on lignin conversion

Bimetallic catalysts, also known as alloy catalysts, was first discovered by Sinfelt in 1960s,\textsuperscript{38} this type of catalysts are prepared by mixing two metals into a intermetallic catalytic system.\textsuperscript{39} This form of catalytic system is expected to have the combined catalytic characteristic from their original monometallic form and/or novel properties from their monometallic catalyst form. For example, Hongliang et al. describe a bimetallic catalytic system, using Fe, Cu, or Ni co-loaded with Ru for lignin hydrodeoxygenation (HDO) process. Although Ru is an excellent catalyst for HDO, by adding a second metal like Ni, the HDO catalytic process activity was increased with a reduced catalysts cost.\textsuperscript{43} Since a large group of heterogeneous catalytic systems are rely on noble metal, co-loaded metal such as Fe, Cu, or Ni to reduce the cost and add addition functionality. A summary of literature indicates that bimetallic catalysts can be created to produce a bifunctional catalyst system which can overcome the disadvantage that a single metal catalyst has, combing the activity of multiple metals.

Based on the above, the ability of CuPMO effectively perform reforming reactions of MeOH for in-situ hydrogen productions and a review of the literature that suggest nickel is more active for aryl-ether hydrogenolysis than copper, we decide to create a Cu/Ni bimetallic system with hydrotalcite as support. The hypothesis is that a bimetallic will optimize reforming reactions to provide a hydrogen source and hydrogenolysis reactions of lignin disassembly. This thesis will mainly focus on two objectives:

- **Objective 1** will focus on making porous metal oxides catalysts with copper, nickel, bimetallic copper and nickel, and mixture of copper-doped porous metal
oxides and nickel-doped porous metal oxides and characterizing the catalyst to understand metal particle size and elemental composition.

- **Objective 2** will focus on performing methanol reforming and metal-catalyzed hydrogenolysis of aryl ethers by analyzing liquid and gas product of reactions with porous metal oxides catalysts with copper, nickel, bimetallic copper and nickel, and mixture of copper-doped porous metal oxides and nickel-doped porous metal oxides. These reactions will be assessed to determine how reaction pathways and kinetics change with different catalyst.

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Chapter II: Bimetallic Catalyst for Lignin Model Compound

Depolymerization

Abstract

The production of renewable aromatics from lignin via reductive cleavage without the addition of an external hydrogen source requires a catalyst effective at both the production of hydrogen and hydrogenolysis of aryl-ether lignin linkages. While Cu-doped porous metal oxide (CuPMO) catalyzes methanol reforming into hydrogen and hydrogenolysis of aryl-ether lignin linkages, the temperature required for sufficient catalytic activity leads to uncontrolled secondary reactions and product proliferation. As a result, CuPMO, Ni-doped porous metal oxide (NiPMO), and CuNi-doped porous metal oxide (CuNiPMO) catalyst prepared, characterized, and compared through an experimental evaluation of reforming activity for hydrogen production and hydrogenolysis activity using a lignin model compound. Global fitting analysis methods were used to understand the evolution of key intermediates and products and to determine the rate constant and activation energies for each step in the reaction network. We eventually found that Cu/Ni doped on the same base support will form into a Cu/Ni alloy after reduction, and new CuNiPMO has a smaller particle size and a larger dispersion rate. CuNiPMO also shows better reforming ability than both CuPMO and NiPMO, and it require less energy for PPE hydrogenolysis process compared to CuPMO and physically mixed form of CuPMO and NiPMO.
2.1 Introduction

The need to produce chemicals and materials from renewable sources in an environmentally responsible matter motivates research into the use of alternatives to petrochemical feedstocks.\textsuperscript{1} An important part of a global shift towards more sustainable technologies is more efficient use of lignocellulose and large-scale development of biorefineries.\textsuperscript{2} A biorefinery combines thermal, chemical and biological conversion processes to efficiently utilize all of the materials and energy contained in lignocellulosic biomass.\textsuperscript{3} However, utilizing lignocellulose-derived carbohydrates for bioethanol production generates similar amounts of lignin as a by-product which is either discarded or burned to recover low-grade heat.\textsuperscript{4} To improve the economic competitiveness and reduce the environmental footprint of such biorefineries technologies are needed that improve biomass-based product yields and selective. Simply stated, this implies obtaining greater value from lignin.

Lignin is composed of three major aromatic monomers based on hydroxycinnamyl alcohols and linked randomly with several linkages\textsuperscript{5, 6}. Lignin usually act as a part of interlaced network around cellulose in cell wall with the function of supporting water transportation and plant protection\textsuperscript{7, 8}. Coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) are the three major lignin monomers\textsuperscript{9, 10}. Two major types of lignin

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure2.1.png}
\caption{Aryl-ether (\(\beta\)-O-4, \(\alpha\)-O-4, \(\beta\)-5, and 4-O-5) linkages in lignin.}
\end{figure}
linkages, those mediated through carbon-oxygen (i.e. $\beta$-O-4, $\alpha$-O-4, $\beta$-5, 4-O-5 in Figure 2.1) and carbon-carbon (i.e. 5-5, $\beta$-1, $\beta$-5, $\alpha$-1) linkages. The abundant carbon-oxygen or aryl-ether linkages in lignin provide a pathway for lignin depolymerization.\(^{11}\)

By breaking these ether linkages at relatively low temperatures, lignin depolymerization can be accomplished while preventing secondary reactions that decrease desired product selectivity and yield of useful aromatic products.

Various of catalytic systems have been developed for lignin depolymerization including heterogeneous homogeneous metal catalytic systems\(^{12-14}\). Among these, noble metals, such as Pt, Pd, Rh-Co, had been used for lignin conversion while non-noble metal catalytic systems, such as those using Fe, Cu, Ni, have also developed in order to reduce the production cost.\(^{15, 16}\) Song et al. observed that the conversion of lignosulfonate to organic liquids and selects for propylguaiacol and 4-ethylguaiacol depend both on the metal and the choice of support.\(^{17}\) Often, bimetallic catalysts, prepared by mixing two different metals into a single catalytic system,\(^{18}\) are used to provide altered or bifunctional catalytic ability. Bimetallic catalytic systems have been used widely in petroleum industries for the reaction process such as hydrogenolysis and reforming reactions, and have also been designed for lignin depolymerization.\(^{19}\) Bimetallic catalytic system, such as the Ni-Pd bimetallic catalyst for lignin hydrogenolysis s reported by Bing Xing et al.\(^{20}\) and Cu-Ni-Al catalyst system for reported by Xiaoming et al.\(^{21}\), can be found in literature. This chapter reports the synthesis, characterization, and use of a bimetallic catalyst for lignin depolymerization.
Porous Metal Oxide Catalyst

A copper-doped porous metal oxide (CuPMO) was prepared by impregnation and calcination of a copper-doped 3:1 Mg:Al layered double-hydroxide or HTC. Ford et al. found that the most effective composition had 20% of the Mg\(^{2+}\) replaced by Cu\(^{2+}\) (Cu\(_{20}\)PMO).\(^{22}\) In addition to catalyzing aryl-ether hydrogenolysis, Cu promotes alcohol reforming and water-gas shift reactions. The resulting H\(_2\) provides the necessary reducing equivalents for hydrogenolysis, hydrodeoxygenation, and hydrogenation. In the case of lignin depolymerization catalyzed by CuPMO, our group have since hypothesized that non-catalytic solvolysis causes lignin fragmentation in the alcohol solvent, yielding soluble lignin oligomers more capable of transport into the pores of and interactions with the surfaces of CuPMOs. Most importantly, the catalyst converts lignin into organic liquids without coke or char formation.

A key problem in the application of CuPMO to depolymerize lignin is aromatic ring reduction and the resulting product proliferation. It is clearly desirable to target aryl-ether cleavage and deoxygenation of lignin while suppressing reduction and other reactions of the aromatic rings.\(^{22,23}\) Under the typical conditions, lignin hydrogenolysis with CuPMOs in supercritical methanol (sc-MeOH) produces a complex mixture of mostly alkyl alcohols and ethers. However, our group has found that dimethyl carbonate (DMC) will O-methylate phenolic hydroxyls, and that the resulting aromatic methyl ethers are much less susceptible to arene hydrogenation than are their aromatic alcohol counterparts, thus improving selectivity toward production of aromatics.\(^{24}\)

A CuPMO performs several functions in lignin disassembly, including (1) H\(_2\)
generation by alcohol reforming; (2) base-catalyzed solvolysis of insoluble lignin to soluble and catalysts accessible fragments; (3) hydrogenolysis of aryl-ether linkages; and (4) base-catalyzed alkylation of phenolics. While it is remarkable that a single-component catalyst is capable of all of these functions, it is very likely that CuPMO is not the optimum catalyst for each function individually. Higher reactivity, especially in the critical hydrogenolysis steps, has been reported for Ni-based catalysts in H$_2$-promoted lignin disassembly,$^{17,25}$ although preliminary experiments with a Ni-doped PMO catalyst (NiPMO) did observe activity for lignin model compound disassembly. We have observed that Ni-alumina provides much faster rates of lignin hydrogenolysis than Cu-alumina on aryl-ether model compounds, but that the Ni-alumina does not catalyze alcohol reforming to produce H$_2$ efficiently. Therefore, the rationale for using a bimetallic catalyst is that the presence of Cu will preserve reforming activity, while the addition of Ni will increase hydrogenolysis rates. In the reaction of hydrocarbons, Cu partially suppresses the hydrogenolysis activity of Ni,$^{26,27}$ thus we expect to find rates that are intermediate between those that are characteristic of the Cu and Ni monometallic systems. However, Cu also exerts a beneficial effect on Ni stability,$^{28}$ making it easier to keep Ni in the reduced active state and preventing coke formation. This is an important consideration for oxygen-rich feeds such as lignin. Thus, our research aims to investigate an bimetallic PMO catalysts with doped with both copper and nickel to test these hypothesis on a lignin model compound 2-phenoxy-1-phenylethanol (PPE) in methanol. Four catalytic systems were tested: (1) Cu-doped (CuPMO), (2) Ni-doped (NiPMO), (3) Cu/Ni-(1:1)-doped bimetallic (CuNiPMO) and
2.2 Materials and Methods

2.2.1 Materials

Nitrite acid (HNO₃), copper nitrate (Cu(NO₃)₂·3H₂O), nickel nitrite (Ni(NO₃)₂·6H₂O), synthetic hydrotalcite (Mg₆Al₂(OH)₁₆CO₃·4H₂O), phenol (98+%), 1-phenylethanol (98+%), acetophenone (98+%), and 1-propanone-1-phenyl (98+%) were purchased from Sigma-Aldrich. Solvents including decane and methanol were purchased from Sigma-Aldrich. 2-Phenoxy-1-phenylethanol (PPE, 97+%) was purchased from ArkPharm (Arlington Heights, IL).

2.2.2 Porous Metal Oxide Preparation

Copper and/or nickel was impregnated into commercially available synthetic HTC. The mass of metal impregnated on the HTC surface was ~5% of the total mole of metal (moles of Mg+Al) in the catalyst. HTC catalysts were prepared with Cu alone (CuPMO), Ni alone (NiPMO), Cu and Ni (Cu:Ni=1:1 mol/mol, CuNiPMO) and CuPMO/NiPMO 1:1 mass physically mixed form (CuPMO/NiPMO). HTC powder (10 g) was stirred with an aqueous solution metal solution containing Cu(NO₃)₂·3H₂O (0.8 g), (Ni(NO₃)₂·6H₂O (0.98 g), or Cu(NO₃)₂·3H₂O (1.59 g) and (Ni(NO₃)₂·6H₂O (1.92) in 100 ml of degasses DI water in a sealed vessel under vacuum for at 2 h. The suspension was ultrasonicated for 2h and the water removed under vacuum and rotary evaporation.
at 70°C. After evaporation, the catalyst was dried at 90 °C overnight and ground into a fine powder. Catalysts were calcined in air at 460°C for 15 h following Ford et al. The catalysts were then reduced at 550, 650, 750, and 800 °C for 4h under 10% H₂/N₂ gas flowing at 35 mL/min.

2.2.3 Depolymerization of 2-Phenoxy-1-phenylethanol (PPE)

2.2.3.1 Bomb Batch Reactions

Batch reaction without the addition of external hydrogen were conducted in a 10 mL stainless steel bomb reactors (Figure 2.2) built according to specification provided by Ford et al. MeOH with 0.06 wt% decane (3 ml), PPE (53 mg), and catalyst (10 mg) were added to each reactor. Sealed the reactors were heated in an oven set to 250, 270°C, or 310 °C residence times of 0.5, 1.5, 2, 3, and 4h for CuPMO; 1, 2, 4, 8, and 16 h for NiPMO, CuNiPMO, and CuPMO/NiPMO. After the reactions were finished, the reactors were put into an ice bath. A series of reactions with no catalyst and undoped PMO catalyst were also conducted.
2.2.3.2 Parr Reactions

Batch reaction in a continuous stirred tank (Parr) reactor Reaction system with the addition of external hydrogen were conducted in a 300 mL reactor. At the start of each reaction the reactor was purged with nitrogen and pressurized with 500 psi hydrogen. MeOH (20 mL) with 12 µL decane, PPE (353 mg), and catalyst (66.7 mg) were added to the reactor. The reactor under stirring was heated to 250 °C for 0.5 h.

2.2.4 Gas Production Collection and Characterization

Gas generate from the reaction will be collected for gas chromatography with thermal conductivity detector (GC-TCD) analysis. Gas generated from reaction will be collected by gas collection apparatus, built according to specification provided by Ford et al^{22,23}, using a balloon to connect the gas. The volume of gas produced was measured based on volume displacement of the inflated balloon. The Gas product will be stored in a Headspace Screw-Thread Vials. The vials will be partially filled with water and stored upside down to prevent possible gas leaking. 100 µL of gas product was manually injected into the GC-TCD (GC, 7890B, Agilent Technologies) with inlet temperature set at 225 °C and 7 mL/min carrier gas flow rate. The GC column Supelco (Carboxen-1010 PLOT column; ID: 0.32 mm; film thickness: 15 µm, and length: 30 m) temperature ramp started at 35°C, rising to 235 °C. Gas products were identified and quantified by the standard gas mixture comprising CO, CO₂, and H₂, in nitrogen (custom mixed by Scott Specialty Gases; Plumsteadville, PA).
2.2.5 Liquid Production Collection and Characterization

The liquid product from each reaction was collected using vacuum filtration and 0.45 μm nylon filters. The product was analyzed using gas chromatography mass spectrometry (GC-MS) analysis. 1 μL of the GC-MS sample was injected on a modified Agilent GC system 7890A coupled with both an Agilent 5975C mass spectroscopy with triple-axis detector and an Agilent G3461A FID detector with methanizer (Activated Research Company) through an Agilent G3470A Auxiliary Electronic Pressure Control (Aux EPC). GC analysis was performed using an Restek fused silica RTX-50 capillary column (ID: 0.25mm, film thickness: 0.5 μm, and length: 30 m) with the following program: 2 min at 40 °C and then ramped at 5 K/min up to 300 °C for 5 min with helium as a carrier gas (splitting ratio: 10:1). GC-MS data was exported and analyzed through ChemStation Software. Identification of the compounds was carried out by comparing the mass spectra obtained with these from system database (PAL600k).

2.2.6 Metal-doped Porous Metal Oxide Characterization

2.2.6.1 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis was performed with an Optima 7300 DV optical emission spectrometer. The catalyst samples were prepared by digesting a known mass in nitric acid for 24 hours and diluted using 18.2 MΩ deionized water. Reference emission lines were monitored at 1267.079, 308.215, 309.271, 396.152, 219.958, 224.700, 324.754, 327.396, 202. 582, 280.270, and 285.213 nm. Calibration curves were constructed with four solutions (0.1,
1, 10, and 100 ppm) prepared by diluting a standard solution (Inorganic Ventures). Each measurement is the average of three replicates.

2.2.6.2 Electron Microscopy

A JEOL 2100 Field Emission Scanning Transmission Electron Microscope with 200kv acceleration voltage will be used for catalysts surface observation. Gatan 806 HAADF and Gatan 805 BF/DF detector will be used for scanning transmission electron microscopy (STEM), Bruker Quantax detector will be used for Energy Dispersive X-Ray spectroscopy (EDX), and a Gatan GIF Tridiem system will be used for Electron Energy Loss Spectroscopy (EELS) analysis. Calcinated CuPMO, NiPMO and CuNiPMO were analyzed via STEM and EDS whereas the calcined CuNiPMO was analyzed by EELS.

2.2.6.3 Temperature programmed reduction and oxidation

Temperature programing reduction (TPR) methods and data was collected using a Micromeritics AutoChem ii 2920 system with a thermal conductivity detector (TCD) for measuring the H₂ consumption amount. 120 mg calcinated sample for each catalyst were set in a furnace tube with (50 mL/ min) hydrogen (10% H₂/He) flow inside under a linear temperature with 10°C/min up to 800°C. After this procedure, the sample will be cool down and go under 10% N₂O/He mixed gas with the flow rate of (50mL/min) for a superficial oxidation at 80°C for 50 min for the oxidation, of nanoparticle on PMO surface. Then the sample will be reduced by H₂ flow again in order to determine the
amount of metal been doped on PMO surface. Based on the data obtained above, metal particle size and metal dispersion on PMO surface can be calculated.

2.2.7 Global fitting and kinetics analysis

The design of the PPE reaction network proposed for all four catalyst systems were mainly based on (1) previously observed CuPMO catalyzed reactivities: hydrogenolysis, hydrogenation, alkylation, aldol, and etherification and (2) experimental data resulting from reactions of network intermediates including that of phenol, 1-phenylethanol, acetophenone, and 1-propanone-1-phenyl with CuPMO, NiPMO, CuNiPMO, and CuPMO/NiPMO. Phenol, 1-phenylethanol, acetophenone, and 1-propanone-1-phenyl are all reaction network intermediates as determined by GC-MS of PPE reactions with CuPMO, NiPMO, CuNiPMO, and CuPMO/NiPMO. Reactions of reaction network intermediates were conducted in bomb reactors (as described above) with 50 µL of each intermediate with 3 mL MeOH and 10 mg catalyst at 310 °C for 3 h. All of the reactions were assumed to be first order reaction for global fitting process to proposed PPE reaction networks. Global fitting was performed using Matlab code designed to construct kinetic models and estimate kinetic parameters.
2.3 Results

2.3.1 Catalyst Characterization

2.3.1.1 ICP-OES

The theoretical molecular formula for undoped HTC is \( \text{Cu}_x\text{Mg}_x\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4(\text{H}_2\text{O}) \). The observed molar ratios of Cu, Mg, and Al normalized to aluminum were 0.41, 3.02, and 1 as measured by ICP-OES (Table 2.1) for the CuPMO sample which is loaded with 3.8 % catalytic metal. The observed molar ratios of Ni, Mg, and Al normalized to aluminum were 0.33, 2.26, and 1 for the NiPMO sample which is loaded with 4.1 % catalytic metal. Whereas the observed molar ratios of Ni, Cu, Mg, and Al normalized to aluminum were 0.24, 0.27, 3.01, and 1 for the NiCuPMO sample which is loaded with 4.8 % catalytic metal.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Molar % Cu</th>
<th>Molar % Ni</th>
<th>Molar % Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPMO</td>
<td>3.8</td>
<td>0.0</td>
<td>3.8</td>
</tr>
<tr>
<td>CuNiPMO</td>
<td>2.5</td>
<td>2.4</td>
<td>4.8</td>
</tr>
<tr>
<td>NiPMO</td>
<td>0.0</td>
<td>4.1</td>
<td>4.1</td>
</tr>
</tbody>
</table>

2.3.1.2 Chemisorption Results

We use chemisorption for estimating the surface area of these reduced nano particles, especially TPR method. Temperature programmed reduction (TPR) is a method that estimate the reduction temperature of metal catalysts and hydrogen consumption
spectra for CuHTC, NiHTC, and CuNiHTC are shown in **Figure 2.3 (black lines)**. TPR showed that the reduction of copper on the CuHTC starts at around 200 °C and associated with a peak maximum of around 300 °C. The shape and maximum of this major hydrogen consumption peak are characteristic of the reduction of Cu$^{2+}$ to Cu$^{0}$ that is not or very weakly interacting with the HTC support. The reduction behavior observed is very similar to that of pure CuO. The TPR of NiHTC shows multiple broad hydrogen consumption peaks starting at 400 °C and continuing until the highest recorded temperature with peak maxima at 500, 600, and 800 °C. The lowest temperature reduction peak at 200 °C corresponds to the reduction of NiO that is weakly interacting with the support. Higher reduction temperature peaks likely correspond to the reduction of Ni$^{2+}$ in thermally stable phases (e.g., Mg(NiAl)O periclases) due to the strong interactions between NiO and MgO. The TPR of the CuNiHTC is similar to that of the CuHTC, however, the major hydrogen consumption peak maximum has shift to a slightly higher temperature of 250 °C. This suggest that due to interaction with nickel, the reduction temperature of the copper increases. There seems to be at least one addition higher temperature reduction peak for CuNiHTC when compared to CuHTC, presumably from the reduction of nickel.

The accessible Cu or Ni metal surface area was determined by selective oxidation of surface Cu and Ni atoms with N$_2$O on reduced CuPMO, NiPMO, and CuNiPMR, followed by H$_2$ uptake during TPR as shown in **Figure 2.3 (red lines)**. Surface area of the metal nanoparticles, $SA_{metal}$ (m$^2$/g), and metal nanoparticle diameter, $d_{metal}$ (nm) were calculated using Equations 2.1-2.3.
\[ D_{Ni}() = \frac{n_H2 M_{metal} SF}{W_{metal} m_{cat}} \times 100\% \quad \text{Eq. 2.1} \]
\[ SA_{metal}(m^2 g_{metal}^{-1}) = \frac{n_H2 N_A SF}{m_{cat} W_{metal} A_{metal}} \quad \text{Eq. 2.2} \]
\[ d_{metal}(nm) = \frac{6 \times 10^3}{SA_{metal} \rho_{metal}} \quad \text{Eq. 2.3} \]

where \( n_{H2} \) is the amount of \( H_2 \) consumed, \( N_A \) is Avogadro’s number, \( SF \) is the stoichiometric coefficient of the metal reduction reaction, \( m_{cat} \) is the mass of catalyst, \( W_{metal} \) is the weight fraction of metal determined by ICP-OES, \( A_{metal} \) is the areal density of metallic metal, \( \rho_{metal} \) is the bulk metal density, and \( M_{metal} \) is the atomic mass of metal.\(^{30}\) Based on Eq. 2.1-2.3, the nanoparticle size and dispersion (i.e., ratio of surface atoms to the total number of atoms) for CuPMO was estimated as 52 nm and

2\%, while CuNiPMO was 5 nm and 20\%. The hydrogen consumption profile of the NiPMO sample prevented an accurate determination of nanoparticle size and dispersion.

\[ Figure 2.3. \ \text{H}_2\text{-TPR results for (A) CuHTC (red) and CuPMO after N}_2\text{O oxidation (black); (B) NiHTC (red) and NiPMO after N}_2\text{O oxidation (black); and (C) CuNiHTC (red) and CuNiPMO after N}_2\text{O oxidation (black).} \]
2.3.1.3 Electron Microscopy

CuPMO, NiPMO and CuNiPMO was examined by scanning transmission electron microscopy (STEM) while electron energy loss spectroscopy (EELS) was applied to

![STEM Image and Particle Size Distribution](image)

**Figure 2.4** STEM image and particle size distribution for A) CuPMO; B) NiPMO; C) CuNiPMO
CuNiPMO. Figure 2.4 shows High Angle Annular Dark Field image (HAADF) STEM images of CuPMO, NiPMO, and CuNiPMO along with related particle size distribution plots. From Figure 2.4a and b, particles on NiPMO and CuNiPMO have a smaller average particle size and a narrower distribution of particle size compared to particles on CuPMO. Most particles formed on CuPMO were relatively large particles with an average particle size of 47 nm. When in the presence of Ni, most particles sizes were between 0-30 nm with the average particle size for NiPMO and CuNIPMO 22 and 12 nm, respectively. Although the particle size results obtained from STEM results are close to those determine via chemisorption results, supporting the chemisorption particle size and surface area analysis.

The EELS image of CuNiPMO is shown in Figure 2.5 and shows the spatial distribution of Cu and Ni in particle. With Cu shown as blue color and Ni shown as green, EELS indicated the particle on CuNiPMO particles contain an intimate mixture Cu and Ni such as that found in a CuNi alloy instead of individual particles of Cu and Ni decorating the PMO surface.

Figure 2.5 EELS image and Cu/Ni distribution image for CuNiPMO
2.3.2 Catalysts Reduction Temperature Optimization

Due to unpublished data from Dr. Susannah Scott and coworkers (University of California Santa Barbara) on the evolution of CuPMO as a result of exposure to biomass disassembly conditions, we knew that catalyst reduction was required. X-ray absorption spectroscopy showed the gradual reduction of Cu$^{2+}$ and formation of Cu(0) nanoclusters when CuPMO was exposed to sc-MeOH which was supported by powder X-ray diffraction (XRD). Using 2-propanol as both solvent and H$_2$ source, CuPMO previously exposed to sc-MeOH, where Cu(0) nanoclusters had already formed, converted benzyl phenyl ether completely and selectively to toluene and benzene below 200 °C, with just 7% hydrogenation to cyclohexanol, whereas pristine calcined CuPMO without Cu(0) nanoclusters was unreactive at this temperature. Based on this, the formation of Cu(0) nanoclusters are critical for reforming and hydrogenolysis activity. The consequence of this in our system was that reduction using a furnace would be required because for

![Figure 2.6](image.png)

**Figure 2.6** Hydrogen gas generation for all five reduction temperatures of CuPMO and NiPMO after 16h hydrogenolysis reaction.
most conditions the reaction environment would be insufficiently reductive to produce zero-valent particle nucleation.

In order to find a suitable reduction temperature for both Cu and Ni catalytic systems, our group tested 550, 650, 750 and 800 °C as the reduction temperature, evaluating both H₂ generation and PPE conversion. The reduction temperature needs to satisfy two basic requirements: (1) Ni is more active than Cu for the breakdown of PPE; and (2) Cu is activated for MeOH-reforming reaction in order to generate a sufficient amount of H₂. Reduction temperature optimization experiments were designed based on the TPR results from the last chapter. For the CuPMO and NiPMO catalysts, the reduction temperatures were designed as 500, 550, 650, 750 and 800 °C. The reduced catalysts for PPE hydrogenolysis reactions were then weighed, dissolved in methanol,

![Figure 2.7](image-url)

**Figure 2.7** (a) PPE conversion without hydrogen present for all 5 reduction temperatures on CuPMO and NiPMO. Reaction condition: 310 °C reaction temperature, 10 mg catalysts, 3 mL MeOH, 53 mg PPE. (b) PPE conversion with hydrogen present for all 5 reduction temperatures on CuPMO and NiPMO. Reaction temperature: 250 °C reaction temperature, 353 mg PPE, 66.7 mg catalysts, 20 mL MeOH, 0.5 h reaction time
and placed in a sealed bomb reactor under 250 and 310 °C for 1.5, 4 and 16 hours.

According to **Figure 2.6**, reduction temperatures around 850°C have no H₂ generation in observed TCD results, indicating that the CuPMO catalyst reduced under 850°C did not trigger a MeOH-reforming reaction. Simultaneously, a large amount of H₂ is generated in the 550 and 650°C reduction temperature processes; the 750°C cases had the highest H₂ generation, showing that 750°C was the best reduction temperature for CuPMO catalysts. Using CuPMO, the H₂ generation for the 550, 650, and 750°C reduction processes was much higher than those using NiPMO. The following tests evaluate PPE’s hydrogenolysis activity using CuPMO and NiPMO as catalysts, which will be reduced under 550, 650, and 750°C.

At 550 and 650°C, the hydrogenolysis experiments produced much higher PPE conversion ratios when using CuPMO than the processes using NiPMO. Likewise, at 250°C, a low reaction temperature, the PPE conversion reached 60% after a 16h reaction. Conversion results indicated excellent PPE hydrogenolyzing capabilities in CuPMO after being reduced at 550 and 650°C, while the NiPMO cases only yielded 10% PPE conversion for the three reduction processes with a hydrogenolysis reaction temperature of 250°C.

Moreover, PPE conversion improved with increases in reaction temperature and reaction time, as seen in the hydrogenolysis case at 310°C for 16h (**Figure 2.7A**). The lack of H₂ generation likely caused the low PPE conversion of NiPMO, which is vital for hydrogenolysis reactions. However, NiPMO’s conversion capabilities cannot be determined with the insufficient presence of H₂. To evaluate the hydrogenolysis
capabilities of NiPMO catalysts, a new series of reactions will be tested inside parr reactors with a continuous hydrogen gas supply.

In the parr reactors, the reactions were carried out under 500 psi with a supply of H₂ from a hydrogen gas tank. Under this pressure, projected PPE depolymerization processes were expected to be efficient, with a high conversion efficiency of almost 100%. We observed higher Cu activity during PPE bond breaking at a reduction temperature of 550°C than Ni (Figure 2.7B), which did not support the use of Cu/Ni bimetallic PMO-doped catalysts. Here, Ni became more active as the reduction temperature rose at 650, 750, and 800°C. The PPE conversion results showed Ni was even more efficient than Cu, which matched the expected function of Ni in the Cu/Ni bimetallic PMO-doped catalyst. According to Figure 2.6, Cu has no reforming activity at 800°C, and the maximum hydrogen production was achieved at 750°C as a reduction temperature. This trend established the 750°C reduction temperature as the best choice for both Cu and Ni to serve their functions in the Cu/Ni bimetallic PMO-doped catalyst. Therefore, 750°C will be chosen as the reduction temperature of the Cu/Ni bimetallic PMO-doped catalyst for the following experimental work.

2.3.3 Hydrogen Production

Gas product analysis, using GC-TCD to determine the concentration of CO and H₂, was used to imply the activity of MeOH reforming for CuPMO, NiPMO, and CuNiPMO. Control experiments with no catalyst added or PMO with no catalyst was tested. The results showed no gas generation which means that the MeOH reforming
reaction could not happen without the presence of reduced metal-doped PMO catalysts.

At 310 °C for 4 h, CuPMO generated 0.54 mmol of H\textsubscript{2} in excess of the H\textsubscript{2} consumed by any potential PPE reactions and 0.39 mmol of CO as shown in Figure 2.8. In contrast, at the same conditions NiPMO generated less H\textsubscript{2} and more CO, producing 0.4 and 0.6 mmol of H\textsubscript{2} and CO, respectively. At 310 °C for 4 h, CuNiPMO and CuPMO/NiPMO produced almost twice as much H\textsubscript{2} than either CuPMO and NiPMO, generating significantly H\textsubscript{2} at 16 h than more either CuPMO and NiPMO. Although it is clear that the presence of Ni increases MeOH reforming activity, because CuNiPMO and CuPMO/NiPMO produced similar amount of H\textsubscript{2}, it is not clear that the presence of Ni as a bimetallic or alloy is required. However, a confound factor is metal loading and particle size. Based on ICP-OES and STEM results, there is a 1:2:5 ratio of metal particle surface area for the CuPMO:NiPMO:CuNiPMO. Considering this fact, CuPMO is fairly effective at MeOH reforming compared to NiPMO and CuNiPMO and CuPMO/NiPMO produces far more H\textsubscript{2} than would result from an additive mixing rule.
At lower reaction temperatures (270 and 250 °C), 4 h was in insufficient to produce detectable levels of H\textsubscript{2} for catalyst except for the CuPMO/NiPMO at 270 °C. CuNiPMO showed detectable production of H\textsubscript{2} at 270 °C for 8 h (Figure 2.9). In many cases however, although detectable levels of H\textsubscript{2} were not produced, hydrogenolysis reactions did occurs suggesting sufficient local hydride production from MeOH reforming occurred to convert some amount of PPE.

**Figure 2.8.** Gas product concentration at 310 °C for all 4 catalytic systems: (A) CuPMO for 0.5-4 h; (B) NiPMO for 1-16 h; (C) CuNiPMO for 1-16 h; and (D) CuPMO/NiPMO for 1-16 h.
2.3.4 Reaction Networks

There are nine major products identified by the GC-MS software pal600k spectral database in the PPE depolymerization process using all four catalysts. Peaks unidentified by the database were excluded from the analysis, and the major products are shown in Figure 2.10.

![Reaction Network Diagram](image)

**Figure 2.9** Gas production for the CuNiPMO and CuPMO/NiPMO at 270°C.

**Figure 2.10** Major products from PPE depolymerization in all four catalytic system.
Based on Ford and Yong’s related reaction network, our group formulated some initial projections of our reaction network’s structure. Yong et al. show that thermal cleavage of PPE through homolysis can directly lead to the formation of phenol and 1-phenylethanol (Figure 2.11).

Derived from a blank experiment with non-metal-doped PMO, the reaction conditions in this study showed that the PMO base causes negligible \( \beta-O-4 \) cleavage. (Figure 2.12)\(^{29, 31} \) As a result, we believe that PPE \( \beta-O-4 \) bond hydrogenolysis in the presence of metal catalysts will lead to the formation of phenol and 1-phenylethanol.

From the structure of acetophenone and 1-phenylethanol, our group determined that a simultaneous hydrogenation and dehydrogenation reaction could occur between these two products, establishing a quasi-equilibrium. Similarly, for some other catalyst system, when there’s more acetophenone been generated than 1-phenylethanol at the same time interval in the PPE hydrogenolysis process; we assume that acetophenone is

![Chemical structures](image)

**Figure 2.11** \( \beta-O-4 \) cleavage of PPE hydrogenolysis process and reverse reaction between 1-phenylethanol and...
produced directly from PPE hydrogenolysis.

Figure 2.12 GC-MS results for no metal doped PMO as catalyst, in 3 ml MeOH, 310°C for a 4-hour reaction time; very little phenol had been observed, indicating that PMO bases are not the major cause of β-O-4 cleavage.

Since the other products contain by-products and limited reference material for elucidating the reaction route, we used chemical analyses and mid-product tests to build the reaction network among all products in these reaction systems. Compared to the other products, phenol, 1-phenylethanol, acetophenone, and 1-propanone-1-phenyl remained in high concentrations in all four catalytic systems.

We selected 50mg of these four mid-products and placed them into 3 mL of MeOH at a reaction temperature of 310°C for 3 hours in each catalytic system. Afterward, we collected the supernatant for GC-MS analysis for product identification (the GC results of these experiments will be shown in the appendix).
In all four catalytic systems, anisole and o-cresol were observed as phenol products. Since these products did not appear in any other tests, we conclude that the alkylation reaction with MeOH will lead to the formation of o-cresol from phenol, and the etherification of phenol will lead to the formation of anisole (Figure 2.13).

**Figure 2.13** Reaction route for phenol and reverse reaction between acetophenone and 1-propanone-1-phenyl.

Apart from phenol and its products, all the remaining major PPE depolymerization products for 1-phenylethanol and acetophenone test results can be observed as the product from 1-phenylethanol and acetophenone. The presence of acetophenone and 1-phenylethanol as each other’s products confirms our assumption of a reverse reaction (hydrogenation and dehydrogenation). Furthermore, acetophenone was observed as a product of 1-propanone-1-phenyl in the four catalytic systems’ 1-propanone-1-phenyl-tests; this implies a reverse reaction between 1-propanone-1-phenyl- acetophenone.
Through a standard alkylation reaction, acetophenone is converted into 1-propanone-1-phenyl, and the 1-propanone-1-phenyl aldol reaction leads to the reverse reaction of acetophenone (Figure 2.13). The other two products, α-Ethylbenzyl alcohol and α-Propylbenzyl alcohol, were also observed from the 1-propanone-1-phenyl test in all four catalytic systems. Since the alkylation of α-Ethylbenzyl alcohol should lead to a ring formation instead of side-chain formation, the α-Propylbenzyl alcohol observed should result from an aldol reaction MeOH and hydrogen from acetophenone. The final undiscussed product is ethylbenzene which arises from the hydrogenolysis process of 1-phenylethanol. The complete reaction network for CuPMO, NiPMO, and CuPMO/NiPMO is shown in Figure 2.14.

Figure 2.14: PPE depolymerization reaction network for the CuPMO, NiPMO, CuPMO/NiPMO reaction systems.
In these three catalytic systems, the acetophenone concentration is significantly higher than that of 1-phenylethanol. This trend indicates the direct production of acetophenone is from PPE hydrogenolysis. Via the bimetallic catalytic system, CuNiPMO's concentration of 1-phenylethanol is higher than acetophenone, which produces a different reaction network, as shown in Figure 2.15.

![Figure 2.15: PPE depolymerization network for the CuNiPMO reaction system.](image)

2.3.5 Global Kinetic Fitting

PPE was subjected to reaction in MeOH with CuPMO, NiPMO, CuNiPMO, and CuPMO/NiPMO at three different reaction temperatures of 310, 270, and 250 °C collecting liquid and gas products at multiple reaction time points. Each reaction was conducted in triplicate. In addition, a series of control reactions were also conducted including PPE with no catalyst and PPE with non-metal doped PMO at 310 °C for 4h. Both control experiments showed no reaction with a nominal PPE conversion.
suggesting that a metal-doped PMO catalyst is required for PPE reaction and that non-catalyzed (e.g., hydrolysis or solvolysis) or PMO base-catalyzed reaction pathways are not involved in the initial PPE aryl ether cleavage. Due to the hydrogenolysis activity of CuPMO, reaction time points for reactions with CuPMO were limited to 0.5, 1, 2, 3, and 4 h; while reactions with NiPMO, CuNiPMO and CuPMO/NiPMO were collected at 1, 2, 4, 8, and 16 h.

A reaction network was constructed based on (1) previously observed CuPMO catalyzed reactivities: hydrogenolysis, hydrogenation, alkylation, aldol, and etherification and (2) experimental data resulting from reactions of network intermediates including that of phenol, 1-phenylethanol, acetophenone, and 1-propanone-1-phenyl with CuPMO, NiPMO, CuNiPMO, and CuPMO/NiPMO.22, 30-32 Due to methylation, O-methylation, and hydrogenation reactions, the solvent contributes to the product mass. Nevertheless, the molar balance over the course of the reaction was greater than 90% for most conditions. The reaction conditions with lower molar balances were those with showing small GC-MS peak at 10-18min retention times. In those cases, the product displayed several small peaks that were not identified too small to quantify reliably, so lower molar balances are largely attributed to product proliferation.

The temporal data obtained from GC-MS analysis of liquid product was evaluated by global kinetics analysis using the Matlab code designed to estimate the reaction rates for interconnected catalytic pathways from PPE through detected and expected intermediates to detected products. All reactions in the reaction network were assumed
to be a first order reaction. Although this assumption may not be completely accurate and neglects potential transport-limitations, this modeling framework should be sufficient to explain the defining trends in the observed data. The time course of major intermediate and products from PPE as well as their predicted concentrations from the kinetic model are shown in Figure 2.16.

CuPMO shows greatest activity for PPE conversion showing up to 90%

![Figure 2.16](image-url)
conversion in 4 h with a high concentration of phenol, acetophenone and 1-phenylethanol at. PPE conversion with NiPMO only reached 15% in 4 h and 43% after 16 h. The reduced activity of NiPMO is likely associated with insufficient MeOH reforming and H₂ production. PPE conversion with CuNiPMO reached 16% in 4 h and 52% after 16 h; while reaching 38% in 4 h and 45% after 16 h for CuPMO/NiPMO.

After long time reaction, the PPE conversion can reach to 50%, which is better than NiPMO system. Still in short time reaction scale, bimetallic catalysts and physically mixed catalysts group are still not active like CuPMO group. It is still remaining unclear that CuNiPMO and CuPMO/NiPMO have such a low PPE conversion result when there’s relatively high amount of H₂ been generated (Figure 2.16 c-d).

In 270°C and 250°C reaction temperatures, there’s negligible PPE conversion for NiPMO system, and for CuPMO, CuNiPMO and CuPMO/NiPMO system, the conversion of PPE in low temperature is between 10%-20%, which indicates that these catalytic systems are not quite active in low reaction temperature. Conversion plots of 270°C and 250°C can be found in appendix.
2.3.6 Activation Energy

Since fitting plot can only provide the information such as product concentration changing and PPE total conversion, we still need to understand the energy cost of each reaction for all four catalytic systems. Rate constants of each reaction can be calculated and recorded through Matlab software, the rate constant forms are shown in the appendix. Based on the rate constants from three different reaction temperatures, the activation energy for most catalytic systems can be calculated, except for NiPMO system which only remain active on 310°C reaction temperature. Detailed activation energies are shown in Table 2.2.

**Table 2.2 Activation Energy Value for CuPMO, CuNiPMO and CuPMO/NiPMO**

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<tr>
<th>Reactions</th>
<th>Activation Energy (KJ/mol)</th>
</tr>
</thead>
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<td></td>
<td>CuPMO</td>
</tr>
<tr>
<td>PPE Hydrogenolysis</td>
<td>83.0</td>
</tr>
<tr>
<td>1-Phenylethanol Hydrogenation</td>
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<td>Acetophenone Oxidation</td>
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<td>Phenol Alkylation</td>
<td>18.0</td>
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<td>1-Propanone-1-Phenyl Retro Aldol</td>
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</tr>
<tr>
<td>1-Propanone-1-Phenyl Hydrogenation</td>
<td>24.0</td>
</tr>
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</table>

Despite that the CuPMO group provide a result with high PPE conversion in short time, the activation energy data shows that after co-doped with Ni, the Cu/Ni bimetallic catalyst system require significant less energy to breaking bonds compare to CuPMO and CuPMO/NiPMO at most reaction. For example, aldol reaction, hydrogenolysis reaction under CuNiPMO system can be mostly taken place with relatively low energy.
request compared to CuPMO and CuNiPMO. Low energy request means after adding Ni to CuPMO system, the ability of breaking bonds for CuNiPMO is actually increased by Ni. Moreover, the low activation energy of CuNiPMO compared to CuPMO/NiPMO indicates the advantage of CuNi alloy on reducing energy cost compared to physically mixture of CuPMO and NiPMO system.

2.3.7 Effect of Hydrogen Addition

Since we suspected that PPE aryl ether cleavage was rate-limited by in-situ H2 generation, we used a Parr stirred batch reactor pressurized to 500 psi to more aptly assess hydrogenolysis ability. Under 500 psi hydrogen pressure, the PPE conversion quickly reaches 100%, so the Parr system had been set for 250°C reaction temperature for 0.5 h reaction, with 20 mL MeOH. 353 mg PPE, 66.7 mg catalysts, and 0.06% of

![Graph showing product concentration of Parr reactor reaction represent in carbon amount](image)

**Figure 2.17** Product concentration of Parr reactor reaction represent in carbon amount
decane as internal standard for GC analysis. The Parr reactor results are shown in **Figure 2.17**.

From **Figure 2.17**, there’s actually quite similar for CuPMO, CuNiPMO and CuPMO/NiPMO in total PPE conversion and product generation. But for NiPMO system, there’s significant more PPE conversion, more secondary product been generated compare to other three catalytic system. Which shows that with enough hydrogen present, NiPMO more efficiently cleaves aryl ether linkages than the other catalytic systems.

### 2.4. Conclusion

PPE conversion results without H₂ present from CuPMO reaction group confirmed the ability of CuPMO on MeOH reforming reaction, compare to NiPMO group, CuPMO is well at reforming reaction and provide enough H₂ for PPE hydrogenolysis process. NiPMO group with hydrogen present have a significant high conversion than other three catalytic group, with more products generated, this confirmed that NiPMO is better at breaking PPE when there’s enough hydrogen present. After combing two metals together in a CuNi bimetallic form, from the EELS image and STEM image, we confirmed the formation of CuNi nanoparticle on PMO surface with a significant smaller particle size and well dispersion rate. New CuNiPMO catalyst is better at MeOH reforming than any single metal catalyst, and it shows better PPE conversion ability compared to single NiPMO catalysts. Though it is still remaining unclear that
CuNiPMO shows less ability on PPE depolymerization with enough H\textsubscript{2} present, CuNiPMO require less energy than CuPMO and CuPMO/NiPMO on most product generation reaction routes, shows that adding Ni to the system has lower the energy request for each reaction in the system.

Reference

10. Whetten; Ross, W.; MacKay; John, J.; Sederoff; Ronald, R. J. A. R. o. P. P.; Biology, P. M., RECENT ADVANCES IN UNDERSTANDING LIGNIN BIOSYNTHESIS. 1998.


23. Barta; Katalin; Bernt; Christopher; M.; Barrett; Jacob; A.; Bottari; science, G. J. C.; technology, Mapping reactivities of aromatic models with a lignin disassembly catalyst. Steps toward controlling product selectivity. **2016**, *6* (9), 2984-2994.


29. Barta; Katalin; Bernt; Christopher; M.; Barrett; Jacob; A.; Bottari; Science, G. J. C.; Technology, Mapping reactivities of aromatic models with a lignin
Chapter III: Future Work

One of the major reasons that lignin conversion is difficult and so challenging to investigate on a fundamental level is the high level of structural heterogeneity that inherently defines lignin. The structure of lignin varies from species-to-species, or even plant-to-plant, influenced by genetic, developmental, and environmental factors.\(^1\) To provide the necessary variation in lignin structure required to assess the effect lignin structure and source have on lignin depolymerization, I have already isolated lignin from: (1) southern yellow pine (\textit{Pinus} spp.), (2) yellow poplar (\textit{Liriodendron tulipifera}), and (3) switchgrass (\textit{Panicum virgatum}). Organsolv fractionation was conducted using a procedure outlined by Bozell et al.\(^2\) Yellow poplar lignin is chosen as a hardwood feedstock because it has a high S/G monomer ratio and no detectable H units. Pine, a softwood, alternatively has predominantly almost all G monomers. Switchgrass has a mixture of S, G, and H monomers. I suspect the distribution of H, S, and G monomers and the distribution of lignin inter-monomer linkages will determine the kinetics of lignin depolymerization and the type of products generated.

Lignin catalytic conversion is known to be affected by its molecular and chemical characteristics. I will employ gel permeation chromatography (GPC)\(^3\) to determine the lignin molecular weight. In addition, we will use solution nuclear magnetic resonance (NMR) techniques to characterize the chemical/molecular features of the feedstock lignin. Specifically, several important chemical functional groups can be profiled quantitatively using \(^1\)H NMR, to measure the % carboxylic acid, aldehyde, aromatic,
O-aliphatic, and aliphatic protons. The increased chemical shift dispersion of $^{13}$C NMR makes it useful for both lignin functional group and substructure profiling (i.e., profiling lignin monomer distribution and monomer linkage distribution). Using $^{13}$C NMR, I will quantify 1) S/G/H ratio; 2) degree of aromatic condensation; 3) methoxyl content; 4) β-O-4, β-β, and β-5 linkage content; and 5) aromatic (C-O, C-C, and C-H) carbon content. Phosphorylation of lignin with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP) will be used to measure and profile the aliphatic and phenolic hydroxyl distribution and content based upon $^{31}$P NMR. Finally, 2D $^1$H-$^{13}$C heteronuclear single quantum coherence (HSQC) NMR is established as an effective method for the semi-quantitative determination of lignin monomer distribution and monomer linkage distribution in lignin. The total organic carbon (TOC) content of the lignin will be determined using a TOC analyzer. Lignin depolymerization will be conducted in Swagelok mini-reactors at a 290, 310, 330 °C for 1, 3, and 6 h with CuPMO, NiPMO, NiCuPMO and CuPMO/NiPMO.

Due to the complexity of lignin and its depolymerization products, the product mixture cannot be analyzed to determine specific reaction networks. Instead, it will be analyzed using NMR, GPC, and GC-MS/combustion-FID to understand shifts in functional group distributions and to determine which small molecules are generated. The relevant NMR experiments include: $^1$H and $^{13}$C NMR to quantitatively profile functional groups in the depolymerized products and to understand the effects of different catalysts. $^{12,13}$ $^{31}$P NMR of phosphorylated lignin depolymerization products is particularly powerful in developing an understanding of lignin chain scission. $^{13}$ 2D
\(^{1}\)H-\(^{13}\)C HSQC NMR substructure analysis can be employed to identify which native substructures are disrupted or remain following depolymerization.\(^{14}\) GPC will be used to determine changes in molecular weight upon depolymerization, and can indicate the rate and extent of depolymerization. GC-MS/combustion-FID will be used to identify and profile specific compounds in the depolymerized products (yields will be based on carbon content).

**Outcomes:**

- Comprehensive understanding of the synergistic effects of adding Ni to CuPMO with respect to alcohol reforming, aryl-ether hydrogenolysis, and catalyst stability.
- Detailed characterization of the mechanisms and kinetics of aryl-ether hydrogenolysis and lignin depolymerization as a function of CuPMO, NiPMO, NiCuPMO and CuPMO/NiPMO composition and structure.
- Development of a new abundant metal catalyst with higher activity and stability for depolymerization of waste lignin into aromatic chemicals.

**Reference**

4. Lundquist K, Olsson T NMR Studies of Lignins. I. Signals Due to Protons in
Appendix: Supporting figures for Chapter II

Figure II-1. H$_2$-TPR results for (A) CuHTC (red) and CuPMO after N$_2$O oxidation (black); (B) NiHTC (red) and NiPMO after N$_2$O oxidation (black); and (C) CuNiHTC (red) and CuNiPMO after N$_2$O oxidation.
Figure II-2. STEM image and particle size distribution for A) CuPMO; B) NiPMO; C) CuNiPMO

Figure II-3. EELS image and Cu/Ni distribution image for CuNiPMO
Figure II-4. Hydrogen gas generation for all five reduction temperatures of CuPMO and NiPMO after 16h hydrogenolysis reaction.

Figure II-5 (a) PPE conversion without hydrogen present for all 5 reduction temperatures on CuPMO and NiPMO. Reaction condition: 310 °C reaction temperature, 10 mg catalysts, 3 mL MeOH, 53 mg PPE. (b) PPE conversion with hydrogen present for all 5 reduction temperatures on CuPMO and NiPMO. Reaction temperature: 250 °C reaction temperature, 353 mg PPE, 66.7 mg catalysts, 20 mL MeOH, 0.5 h reaction time.
**Figure II-6.** Gas product concentration at 310°C for all 4 catalytic system: (A) CuPMO gas product concentration in 0.5-4 h reaction time; (B) NiPMO gas product concentration in 1-16 h reaction times; (C) CuNiPMO gas product concentration in 1-16 h reaction times; (D) CuPMO/NiPMO gas product concentration in 1-16 h reaction times.

**Figure II-7.** Gas production for the CuNiPMO and CuPMO/NiPMO systems with a reaction temperature of 270°C.
Figure II-8. Product Test for CuPMO.
Figure II-9. Product Test for NiPMO.
Figure II-10. Product Test for CuNiPMO.
Figure II-11. Product Test for CuPMO/NiPMO.
Figure II-12: PPE depolymerization network for the CuNiPMO reaction system.

Figure II-13: PPE depolymerization reaction network for the CuPMO, NiPMO, CuPMO/NiPMO reaction systems.
Figure II-14: Product fitting plots for CuPMO system
Figure II-14: Product fitting plots for NiPMO system
Figure II-15: Product fitting plots for CuNiPMO system
**Figure II-16**: Product fitting plots for CuPMO/NiPMO system
### Table II-1 Activation Energy Value for CuPMO, CuNiPMO and CuPMO/NiPMO

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<td>CuPMO</td>
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<tr>
<td>PPE Hydrogenolysis</td>
<td>83.0</td>
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<td>1-Phenylethanol Hydrogenation</td>
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### Table II-2 Rate Constant Value for CuPMO system

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Table II-4 Rate Constant Value for CuNiPMO system

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