Catalytic Upgrading of Aromatic Oxygenates Related to Lignin

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CATALYTIC UPGRADING OF AROMATIC OXYGENATES RELATED TO LIGNIN

by

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DEDICATION

To my great-grandmother – I love and miss you every day.
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ABSTRACT

Lignin is one component of lignocellulosic biomass and is the only renewable, naturally-occurring source of aromatics in the world. However, lignin also provides a highly-oxygenated, complex, heterogeneous structure making the procurement of isolated aromatic molecules quite difficult. There has been extensive research in recent years to develop approaches to catalytically breakdown the lignin polymer into monomeric units. This works aims to develop a number of catalytic techniques for the upgrading of these monomeric units of lignin to produce means for producing chemical building blocks as well as suitable fuels from biomass sources.

A method for the silanolysis of alcohols has been developed using a non-corrosive base catalyst, K$_2$CO$_3$. Chapter 2 details the reactions between a variety of alcohols and hydrosilanes to generate silyl ethers under mild conditions. These mild conditions allow for a wide substrate scope of alcohols to be explored due to a high functional group tolerance. Many of the alcohols that have successfully been silylated in this work are aromatic units. In total, 25 silylated alcohols were prepared through use of 5 different hydrosilanes. This silylation process is successful in the presence of reactive C–H bonds. The silylated alcohols prepared in this work have the potential to be used in polymer synthesis as well as to be used in hydrodeoxygenation reactions that would otherwise be difficult to perform.

The aim of Chapter 3 is to explore the hydrodeoxygenation capabilities of the homogeneous transition metal catalysts, (2,2′:6′,2″-terpyridine)nickel(II) hexafluorophosphate and chloro(2,2′:6′,2″-terpyridine)palladium(II) chloride. The latter
exhibited excellent activity and performed completely selective hydrodeoxygenation of benzylic oxygenates under very mild conditions. This catalysis was also observed at room temperature. The results of this work indicate a single-site molecular catalyst, which leads to the complete selectivity and lack of side product formation.

In Chapter 4, the development of heterogeneous single-site molecular complexes is explored for the selective hydrodeoxygenation of benzylic oxygenates. The catalysts prepared are direct modifications to the successful catalyst in Chapter 3. Chloro(2,2′:6′,2″-terpyridine-4′-carboxylic acid)palladium(II) chloride and chloro(-([2,2′:6′,2″-terpyridin]-4′-yl) benzoic acid)palladium(II) chloride, were synthesized and used to modify the surface of amorphous silicon dioxide to generate a hybrid molecular/heterogeneous catalyst. The hybrid catalytic system exhibited excellent activities and selectivities for hydrodeoxygenation while displaying the ability to recycle through multiple catalytic reactions. Spectroscopic techniques indicate that the molecular catalyst is present on the surface of SiO₂ and the formation of unwanted metallic Pd nanoparticles can be avoided. Post reaction analysis of the surface-modified oxide catalysts confirmed prolonged molecular integrity of the catalysts and sustained binding of the catalysts to the oxide surface when nonpolar solvents were employed for reactions.
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CHAPTER 1

INTRODUCTION
Lignin

Biomass is an important feedstock for the production of fuels and commodity chemicals from a renewable resource. Lignocellulosic biomass is composed of three major components: cellulose, which represents 40-50% of biomass present on Earth, hemicellulose, representing another 25-35% of biomass, both of which are primarily composed of complex polysaccharides.\(^1\) The third component is lignin, while representing just 15-25% of the world’s biomass by weight, lignin accounts for 40% of the energy biomass can provide.\(^2\) Lignin is the second most abundant, naturally occurring polymer in the world, however lignin is not used effectively in industry.

Processing of biomass in a biorefinery could be directly compared to traditional oil refineries that are prevalent throughout the world. Unlike crude oil, biomass is one of the most significant renewable resources present on Earth, and the only renewable resource that provides the opportunity to be converted to a useable liquid fuel.\(^3\) The utilization of biomass first requires the conversion of solid biomass into a useable liquid.\(^4\) Another difference in using biomass as a direct competitor to the fossil fuel industry, is the heterogeneous nature of the material itself. Given the variety of structures present within lignocellulosic biomass, the upgrading process is not as straight forward as is seen in oil refineries. Given the above examples, comparing biomass with previously developed petroleum industry is quite difficult. However, biomass sources provide a key component that crude oil is unable to offer. While the crude oil industry requires the functionalization of byproducts, biomass is prefunctionalized, thus potentially requiring defunctionalization in order to form commodity chemicals.

Technologies have been developed to make use of the cellulosic and hemicellulosic components of lignocellulosic biomass, though use of lignin is lacking.\(^5\) Lignin is a
naturally occurring amorphous polymer, which provides structural integrity to plants and is a non-edible component of the biomass. The structure of lignin is composed of a highly complex phenolic polymer derived from three monomeric units: coumaryl, coniferyl and sinapyl alcohol as shown in Figure 1.1. Lignin is one of the few naturally occurring sources of aromatic molecules that is currently known, thus is an attractive precursor for the production of commodity chemicals as well as liquid fuels. As mentioned above, lignin valorization has not received very much attention as compared to cellulose. Given this fact, lignin has the untapped potential to be a source for sustainable production of fuels and bulk chemicals. Generally, lignin is burned as a low value fuel rather than being used commercially due to lignin’s recalcitrant structure. The structure seen in Figure 1.2 is a direct result of a nonuniformly distributed structure possessing a variety of oxygenated functional groups that cannot be treated equally. Further, the linkages between units present in lignin structure can vary greater depending on their source. Among these linkages, are β-O-4, 5–5, β-5, 4-O-5, β-1 and β- β, while the β-O-4 linkage is by far the most dominant within the lignin structure. The structure of lignin offers advantages over the cellulose and hemicellulose portions of lignocellulosic biomass in that lignin offers a more direct route to specialty chemicals.

Figure 1.1: Structures of the three major monomeric components of naturally occurring lignin: coumaryl (Cm), coniferyl (C) and sinapyl (S) alcohol (left to right)
Despite the difficulty in the native lignin structure, a new approach has gained significant research interest in recent years. This new concept called lignin-first has been proposed and extensively studied. This process relies on the stabilization of lignin during fractionation of biomass sources. In doing so, researchers have achieved high isolated lignin yield while maintaining structural integrity. This approach can be described in a general sense, to separate lignin and disassemble the polymer prior to working on the cellulosic components of the biomass. The lignin-first approach has been given a variety of names through recent years such as reductive catalytic fractionation (RCF), early-stage catalytic conversion of lignin (ECCL) and catalytic upstream biorefining (CUB). Although each of these named processes have small changes, they all share the same mechanistic background: the extraction of lignin accompanied by depolymerization and reductive stabilization of reactive intermediates. The development of the lignin-first...
approach has brought lignin valorization to the forefront of energy research, thus allowing further research to take place on the upgrading of depolymerized lignin monomers.

The proposed process for the production of fuels or higher value commodity chemicals from lignin is an approach that requires two concrete steps. First the depolymerization of lignin into smaller subunits is required before making any further modifications. There have been several approaches developed to depolymerize lignin in addition to the lignin-first approach. Catalytic and non-catalytic depolymerizations have been studied such as pyrolysis, oxidation, hydroprocessing acid-catalyzed and base-catalyzed.\textsuperscript{13} Despite differences in the conditions required to depolymerize lignin, the products obtained following a successful depolymerization reaction are cyclic hydrocarbons and aromatics as seen through the presence of the three basic monolignols in Figure 1.1. Furthermore, the approach to obtaining depolymerized lignin is a topic of study as well. Mainly, there are two distinct routes researchers have taken to produce depolymerized lignin. First, metal catalysts have been employed to break down the polymer in the presence of cellulose and hemicellulose. Second, an solvation approach can be taken to separate lignin from the other components followed by catalysis to break down lignin in the absence of other components of biomass.\textsuperscript{6}

Each of the methods for the depolymerization of lignin generally yield the same set of products.\textsuperscript{14-17} This fact opens the door for research to take place on model compounds that resemble that of depolymerized lignin. The second step for the upgrading of lignin to useful chemicals and fuels requires the manipulation or defunctionalization of the aromatic monomers of depolymerized lignin. A variety of techniques have been attempted for the upgrading of lignin, either directly or through the use of model monomers.\textsuperscript{18-20} This work will first discuss the silylation of aromatic alcohols as models for the upgrading of lignin-
derived aromatics to useful chemicals. Additionally, the hydrodeoxygenation of benzylic oxygenated molecules will be discussed as well as catalytic routes to achieve efficient catalysis. Both of the above areas have relevance in the field of lignin valorization towards the production of higher value products and fuels.

**Silylation of Alcohols**

As discussed in the previous section, the depolymerization of lignin has been studied, providing the knowledge of monomeric units to be utilized in upgrading processes. Upon catalytic depolymerization, aromatics that are functionalized with oxygen-containing moieties are yielded. The next step then becomes, what is to be done with these products in an efficient way to afford value-added products. Various methods have been explored to convert lignin to valuable chemicals.\(^6,\) \(^{21}\) Among these methods include catalytic reduction pathways, which can be employed in a variety of ways. Reductive strategies have been used to perform depolymerization of actual lignin through the use of metal catalysis. Despite these strategies being used, conversions of lignin are either low or require extreme thermal conditions in order to generate higher conversions.\(^{22-23}\) Additionally, functional groups such as alcohols, aldehydes and ketones are prime candidates for catalytic reduction as well. In some cases, B(C\(_6\)F\(_5\))\(_3\) (tris(pentafluorophenyl)borane) is used to catalyze the reduction of oxygen containing functional groups in the presence of hydrosilanes.\(^{24-27}\) The catalyzed formation of silyl ethers from hydro- or chloro-silanes in the presence of a catalyst is known as silylation for alcohols and hydrosilylation for aldehydes and ketones. Silylation of oxygenated functional groups that are prevalent in lignin can be realized through this process both for the addition of protecting groups as well as ease of reduction to hydrocarbons. In many cases, the reduction of these substrates down to hydrocarbons takes place on benzylic oxygens, while the presence of phenolic oxygens simply become
silyl ethers and do not react further. Figure 1.3 illustrates the reaction that would take place between a hydrosilane and an oxygenate, displaying the formation of silyl ethers from alcohols and carbonyls. Omitted, however, from these studies is the use of silylated oxygenates as protecting groups to further carry out other chemical processes.

Figure 1.3: General schematic detailing hydrosilylation of oxygenates

The use of silyl ethers can play the role of a protecting group in converting functionalized aromatic alcohols derived from lignin depolymerization into new polymers. Silyl ethers have been employed as a protecting group for radical chain polymerization reactions to form well-defined polymers from renewable resources. Interestingly, these reductive pathways focus on the degradation of lignin, there has been a lack of attention paid to the reductive conversion of model lignin monomers. As shown in Figure 1.2, there is a large number of alkyl-aryl or diaryl ether linkages present that are prime targets for catalytic reduction. Very recently, the reductive degradation of lignin and model compounds was reported through the use of hydrosilanes. Through this process, ether linkages and primary alcohols could be removed, however secondary alcohols were converted to silyl ethers and did not react further. Through this study, it was concluded that reactivity of oxygen-containing functional groups present in vanillyl alcohol, a model lignin monomer, followed a trend. Silyl ethers formed first on phenolic oxygens, followed by the benzylic position and lastly by methoxy linkages on aromatic rings. Further reactivity was not seen on either the phenolic or methoxy linkages, however reduction of the benzylic position to the hydrocarbon is observed only after all three oxygenated species were silylated, this reactivity is detailed in Figure 1.4. The fact that benzylic oxygens are
able to be reduced to hydrocarbons, suggests that under optimized conditions, reduction to hydrocarbons can be realized at phenolic positions as well.

![Reduction trends using silylation of vanillyl alcohol, a model substrate for depolymerized lignin](image)

**Figure 1.4:** Reduction trends using silylation of vanillyl alcohol, a model substrate for depolymerized lignin

There has been attention paid to the catalyzed-protection of alcohols and other oxygenated functional groups.\(^{30-31}\) Further, the solvent-free protection of benzylic alcohols reported with very short reaction times.\(^{32}\) However the literature does not pay particular attention to aromatic alcohols, nor does it address the fact that there are a large presence of both primary and secondary alcohols present in the lignin polymer. This may very well be due in part to the requirement of relatively harsh reaction conditions such as high temperatures, additives and the use of strong bases to activate the substrates. Furthermore, the chemistry for silylation of alcohols has been developed for many years, while the extraction and valorization of lignin is just now coming into the forefront of energy research. Another successful route to the generation of silyl ethers is through the use of chlorosilanes.\(^{32-33}\) The use of chlorosilanes as silylation agents on a large scale is also disadvantageous due to generation of HCl as a byproduct, which requires neutralization in order to obtain products from the reaction. The utilization of silylation protection reactions would require the ability to be used on a large scale if lignin were involved. Though significant work has been put forth towards the generation of silyl protection groups on oxygen-containing functional groups, there remains a need for more efficient processes and the ability to scale those same processes up. Chapter 2 will detail a mild-base catalyzed
silylation of alcohols with an emphasis placed on functional group tolerance as well as aromatic alcohols as seen in lignin monomers.

**Catalytic Hydrodeoxygenation**

A significant amount of work has been put towards developing selective catalytic routes for upgrading of lignin through a variety of methods. As mentioned previously, lignin depolymerization is generally considered the first step in transforming lignin into valuable chemicals and fuels. Although partial deoxygenation has been observed through depolymerization pathways, a significant amount of work has been dedicated to the deoxygenation of model aromatic compounds of depolymerized lignin instead.\textsuperscript{34-35}

Hydrodeoxygenation is just one pathway through which lignin-derived aromatic molecules can be upgraded. Hydrodeoxygenation refers to the removal of oxygen-containing functional groups in the presence of hydrogen gas, while releasing water as the byproduct. Other pathways include hydrogenation, hydrogenolysis, and dehydration, all of which are useful depending on the target of research.\textsuperscript{36} A simple schematic displaying the different pathways from phenol is depicted in Figure 1.5, it is notable that hydrodeoxygenation is the only pathway that the resulting product has maintained aromaticity. There are numerous catalytic studies devoted to determining the best catalytic system for the deoxygenation of aromatic molecules while maintaining aromaticity. The desire for maintaining aromaticity lies in the energy derived from a molecule used for fuel. This value is known as the octane rating of the fuel. On average, aromatic such as benzene, toluene, xylene, ethylbenzene and cumene exhibited higher octane ratings than saturated hydrocarbon rings or chains. It should also be noted that alcohols typically have higher octane ratings as well, however the combustion reaction of alcohols and other oxygen-containing molecules are inefficient and produces toxic chemicals such as formaldehyde.\textsuperscript{37} A combination of higher octane
rating with more efficient combustion reactions drives the desire to produce deoxygenated aromatic molecules from biomass sources.

\[ \text{Figure 1.5: Schematic of common transformations made to aromatic alcohols derived from lignin sources.} \]

A significant portion of hydrodeoxygenation studies have been through the use of heterogeneous, metal nanoparticle catalysts.\textsuperscript{38-39} Typically, metal nanoparticle catalysts exhibit limited selectivity while having high activities, although these activities generally require harsh conditions to achieve.\textsuperscript{40-41} Heterogeneous catalysts typically carry out hydrogenation reactions prior to deoxygenation pathways, as extended metal surfaces (i.e. nanoparticles) are known for hydrogenation of alkenes and aromatics.\textsuperscript{6,42-43} For instance, model lignin monomers such as cresols, anisoles and catechols were either partially or wholly deoxygenated over a sulfided cobalt-molybdenum catalyst with varying selectivity.\textsuperscript{44} Studies on other sulfided CoMo and NiMo catalysts have been known to show high activities for the conversion of guaiacol, although with very low selectivities.\textsuperscript{45} Furthermore, catalyst support generally has not shown to play a significant role in the selectivities of these processes. Alumina-supported molybdenum nitride catalysts also showed high reactivities for the reduction reactions of guaiacol, however selectivities were lacking.\textsuperscript{46} Despite this, there have been a number of reports detailing high selectivities of
heterogeneous catalysts for these processes.\textsuperscript{47} While these successful attempts at selective hydrodeoxygenation pathways, harsh conditions are required.

Another, less-explored approach for the hydrodeoxygenation of aromatics is through the use of homogenous, molecular catalysts. One distinct advantage to using molecular catalysts for organic transformations is the ability to tune reactivity through synthetic modifications to the ligand framework in which the catalyst operates.\textsuperscript{48-49} Unlike heterogeneous catalysts, the use of homogeneous catalysts in an industrial setting is limited due to lack of robustness. Additionally, homogeneous can require complicated separations from the reaction mixture to obtain clean products. Despite this, there have been several examples of deoxygenation of organic molecules through the use of homogeneous catalysts.\textsuperscript{50} Particular attention has been paid to the hydrogenolysis of aryl ethers.\textsuperscript{51-52} The currently available literature does not offer a comprehensive view into the selective hydrodeoxygenation of model lignin monomers. Chapter 3 will discuss the development of a homogeneous palladium catalyst with the capability of performing the selective hydrodeoxygenation of benzylic substrates related to lignin under relatively mild conditions.

**Single Site Molecular Catalysts**

In the previous section, the advantages and disadvantages of both homogeneous and heterogeneous catalysts were discussed. However, there lies the possibility of combining the positive aspects of each catalytic system through the use of single-site molecular catalysts attached to a solid support. Single-site molecular catalysts could be thought of as a hybrid heterogeneous catalyst, with the stability and separation of a heterogeneous catalyst along with the tunability of a homogeneous catalyst. Modifications to ligand frameworks of homogeneous metal complexes are required to accommodate the
construction of single-site molecular catalysts. Development of these synthetically modified catalysts allow for the attachment to solid metal oxide supports, as seen in figure 1.6. A vast majority of the work dedicated to the use of single-site molecular catalysts supported on metal oxide supports are used in electro- and photo-chemical applications.\textsuperscript{53-55}

![Figure 1.6: General structure of a synthetically modified molecular catalyst bound to the surface of a metal oxide support](image)

The above mentioned single-site molecular catalysts are rarely utilized in thermally activated processes, with the exception of cross-coupling reactions through the use of solid supported palladium complexes.\textsuperscript{56-60} As mentioned in the previous section, catalytic hydrodeoxygenation requires selectivity to be a viable candidate to challenge the current fossil fuel industry. The viability of this process would simultaneously require the use of an industrially-friendly catalytic system, something that a homogeneous catalyst would be unable to offer. Thus, catalytic deoxygenation of aromatic organic molecules is a thermally activated catalytic pathway that deserves interest in the field of single-site molecular catalysis. The molecular nature of the catalyst has the potential to provide the selectivity
required to deoxygenate aromatic oxygenates while maintaining the desired aromaticity. Simultaneously, single-site molecular catalysis would provide the ability to separate the catalysts from the reaction mixtures and the robustness required to recycle the catalysts.

Although there is limited knowledge pertaining to the strength and the nature of the binding site between molecular catalyst and solid support, the stability of heterogeneous-molecular catalysts has been brought into question.\textsuperscript{61} It is noted in this review that there needs to be extensive characterization carried out on these hybrid catalyst systems to ensure that the nature of the catalytic active site remains molecular in nature. There are limited characterization techniques available for the determination of the presence of supported molecular catalysts, however characterizing the nature of supported molecular catalysts is important and needs to be addressed. The decomposition of supported molecular catalysts can take place in two ways, first the catalyst can become detached from the surface of the support and becoming solvated in the reaction solvent if soluble, secondarily the metal complex can decompose by losing the metal center similarly to decomposition pathways that are seen homogeneously.\textsuperscript{62-63} It has been reported that surface immobilization of molecular catalysts can prevent the bimolecular nature of decomposition that is commonly seen through homogeneous catalysis.\textsuperscript{64} With that in mind, careful attention needs to be paid towards the decomposition of supported molecular catalysts through the former pathway.

The use of hybrid heterogeneous-molecular catalysts in polar solvents have the potential for ligand-metal dissociation leading to deactivation of the catalyst.\textsuperscript{56-57} Without the requirement of solubility, as see in homogeneous catalytic reactions, these hybrid catalysts can be utilized in non-polar solvents without the worry of deactivation due to solvent effects.\textsuperscript{65} A synthetically modified palladium catalyst from Chapter 3 will be discussed in Chapter 4 for the catalytic hydrodeoxygenation of benzylic oxygenates related
to lignin, with consideration to catalyst characterization and recyclability in a non-polar solvent.
References


CHAPTER 2
MILD SYNTHESIS OF SILYL ETHERS VIA POTASSIUM CARBONATE CATALYZED REACTIONS BETWEEN ALCOHOLS AND HYDROSILANES

1 Adapted from DeLucia, Nicholas A.; Das, Nivedita; Vannucci, Aaron K.; Org. Biomol. Chem., 2018, 16, 3415-3418 with permission from The Royal Chemical Society.
Abstract

A method has been developed for the silanolysis of alcohols using the abundant and non-corrosive base K$_2$CO$_3$ as the catalyst. Reactions between a variety of alcohols and hydrosilanes generate silyl ethers under mild conditions. The use of hydrosilanes lead to the formation of H$_2$ as the only byproduct thus avoiding the formation of stoichiometric strong acids. The mild conditions lead to a wide scope of possible alcohol substrates and good functional group tolerance. Selective alcohol silanolysis is also observed in the presence of reactive C–H bonds, lending this method for extensive use in protection group chemistry.

Introduction

The protection of reactive functional groups, such as alcohols, amines, and thiols, is highly prevalent throughout organic syntheses. In particular, the silylation of alcohols to form silyl ethers is an important reaction in protecting group chemistry.\textsuperscript{1} Hydroxy group protection via Si–O bonds has also extensively been used to alter the steric and electronic properties of substrates.\textsuperscript{1} Silyl ethers have also played a large role in the development of organic semiconducting materials,\textsuperscript{2} been used in the synthesis of medical compounds,\textsuperscript{3} and utilized as directing groups for C–H activation reactions.\textsuperscript{4-5}

Sterically bulky silyl groups have exhibited a desired balance between protecting group abilities and ease of desilylation to reform the alcohol.\textsuperscript{1} Much of the initial reports on the formation of silyl ethers with sterically bulky silyl groups focused on the treatment of alcohols with chlorosilanes, as shown in Figure 2.1 A.\textsuperscript{6} In addition to the moisture sensitivity of the chlorosilanes, this procedure requires an excess of base, such a pyridine or imidazole to neutralize the HCl byproduct.\textsuperscript{7-9} The formation of HCl as a byproduct can also prevent the use of acid sensitive alcohol substrates and limits the practicality of scaling
up the reaction to industrial levels. More recently, silanolysis of alcohols has focused on the use of hydrosilanes in the general form $R_3SiH$ (Figure 2.1 B). This procedure avoids the production of unwanted acid, as $H_2$ is the only byproduct generated. Hydrosilanes are also less sensitive to moisture compared to chlorosilanes. Dehydrogenative silylation of alcohols with hydrosilanes, however, does require a catalyst to promote the reaction.

Figure 2.1: Comparison of silanolysis of alcohols with the use of chlorosilanes versus the use of hydrosilanes.

A variety of catalysts have been explored for the formation of O–Si bonds from alcohols and hydrosilanes.$^{10-21}$ Transition metal catalysts have been used to successfully construct O–Si bonds.$^{10-14}$ These catalysts, which range from rare earth metals such as ruthenium and iridium to earth abundant metals such as nickel and titanium, are not commercially available and have exhibited limited reactivity with tertiary alcohols and bulky hydrosilanes. Lewis acid catalysts, such as $B(C_6F_5)_3$, are commercially available and avoid use of transition metal catalysts.$^{15-17}$ These Lewis acid catalysts have also shown the ability to catalyze reactions involving secondary and tertiary alcohols and bulky hydrosilanes under mild conditions. Lewis acid catalysts, however, are commonly incompatible with Lewis basic functional groups such as pyridine. Alternatively, base-catalyzed dehydrosilylation of alcohols have also been explored.$^{18-20}$ Many of these base-catalyzed studies report harsh conditions such as high temperatures, strong bases, and excess of additives to promote reactivity and are more commonly employed for
hydrosilylation reactions. A recent report, however, showed that the dehydrosilylation of alcohols with hydrosilanes can be achieved under more mild conditions with a catalytic amount of NaOH. The strength of the base catalyst, however, could limit functional group tolerance. There remains a need, therefore, for a mild, catalytic route for the dehydrosilylation of alcohols with a wide functional group tolerance.

The Oestreich group has shown that Cs$_2$CO$_3$ is an effective, mild catalyst for the dehydrogenative coupling of diols with hydrosilanes. The authors showed that with 10 mol% base catalyst and excess hydrosilane, the protection of 1,3- and 1,4-diols could be achieved at room temperature in THF. Utilizing K$_2$CO$_3$ or Na$_2$CO$_3$ as the catalyst resulted in much lower reaction efficiency. In addition, alcohol substrates beyond diols were not reported.

Herein we report the K$_2$CO$_3$ catalyzed dehydrosilylation of a variety of alcohol substrates. The catalyst operates at conditions as mild as room temperature, and the relatively weak base catalyst is compatible with a wide range of functional groups. Alcohols that are sensitive to Lewis acid and strong Lewis base catalysts were successfully silylated. Substrates containing halogen, alkene, and alkyne functional groups all resulted in high yields of dehydrosilylated products without observation of unwanted side products from hydrosilylation. In addition, a variety of hydrosilanes were compatible with this catalytic approach.

**Results and discussion**

Reactions were prepared by adding the chosen silane to a minimal amount of a DMF:THF solvent mixture (1:1, 1mL) containing the alcohol substrate and 20 mol% K$_2$CO$_3$ catalyst. A 1:1 DMF:THF ratio proved to be the optimized solvent over just DMF, just THF, or acetonitrile. Furthermore, a lesser concentration of K$_2$CO$_3$ resulted in
diminished yields, while a greater concentration of the base catalyst did not improve yields beyond what is reported below. A small excess of silane was required to achieve optimized yields, as has been previously observed.\textsuperscript{15, 21-22} All solvents were purchased anhydrous and used without further purification. All glassware and the \( \text{K}_2\text{CO}_3 \) catalyst were dried in an oven to remove residue water. While water does not fully prevent product formation, the presence of water does result in formation of a siloxane.\textsuperscript{15, 21} After the reaction, products were separated using flash chromatography and purity was determined by NMR spectroscopy.

Figure 2.2 shows that this method efficiently dehydrodimethylsilylates phenolic alcohols. Triethylsilane (TES) was chosen as a readily available and bulky silane that has not been extensively explored for silylation reactions. The moderately bulky nature of TES balances the ease of silylation with the ability to later remove the silane protecting group.\textsuperscript{15} Triethylsilylation of unsubstituted phenol occurred with a 95\% yield (entry 1). Phenolic alcohols with substitutions of both electron donating and withdrawing groups at the para position (2c – 4c, 5) all resulted in excellent yields. Substrates with functional groups at the ortho- and meta- positions also were successfully silylated with yields between 62\% and 98\%.

\[
\begin{array}{cccc}
\text{Entry} & \text{Reaction} & \text{Yield} \\
1 & \text{OH} & \text{K}_2\text{CO}_3 (20 \text{ mol\%}) & \text{OSi(Et)}_3 \text{H}2 \\
2a & \text{H}_3\text{C} & \text{o-} & 72\% \\
2b & \text{Br} & \text{m-} & 87\% \\
2c & \text{MeO} & \text{p-} & 99\% \\
3a & \text{Br} & \text{o-} & 84\% \\
3b & \text{MeO} & \text{m-} & 91\% \\
3c & \text{MeO} & \text{p-} & 99\% \\
4a & \text{O}_2\text{N} & \text{o-} & 87\% \\
4b & \text{O}_2\text{N} & \text{m-} & 98\% \\
4c & \text{O}_2\text{N} & \text{p-} & 99\% \\
5 & \text{OH} & \text{p-} & 98\% \\
\end{array}
\]

Reactions performed at 60 °C except for substrates 2a-e which were performed at 25 °C. 3 equiv of TES. 18-hour reaction time.

\textbf{Figure 2.2.} \text{K}_2\text{CO}_3 \text{ catalyzed triethylsilylation of substituted phenolic alcohols.}
With knowledge that K$_2$CO$_3$ is an efficient catalyst for the triethylsilylation of phenolic alcohols, we looked to show that this procedure was applicable for a range of different silanes. The steric and electronic character of silanes will have an effect on the reactivity. The ease of silylation and subsequent deprotection of alcohols is dependent on the identity of the silane.\textsuperscript{1} Figure 2.3 illustrates that K$_2$CO$_3$ is a compatible catalyst for various silylation reactions. Yields for the protection of phenol with silanes that vary in steric bulk and electronic character were nearly quantitative with the exception of tri-isopropyl silane. For product 8 excess silane dimer was observed in the mass spectrum, which is what likely led to the lower (67%) yield.

![Figure 2.3: K$_2$CO$_3$ catalyzed silylations of phenols through the use of various hydrosilanes.](image)

Reactions performed at 60 °C. 3 equiv of SiR$_3$. 18-hour reaction time.

To further explore the scope of the K$_2$CO$_3$ catalyzed dehydrosilylation of alcohols, a range of alcohol substrates were examined. Both triethyl- and triphenylsilane (TPS) were used to achieve high yields of the desired silyl ethers. Unsubstituted and 4-substituted benzyl alcohols were successfully silylated (products 10 and 11). Substrates containing unsaturated carbon atoms, such as cinnamyl alcohol (product 13) were also successfully dehydrosilylated without observing any hydrosilation products. This catalytic procedure was also successful with both secondary (product 14) and primary (product 15) aliphatic alcohols. Lewis acid sensitive groups such as pyridine (product 16) and furan (product 17)
also underwent efficient dehydrogenative silylation. The functional group tolerance of this catalytic approach was further shown with the nearly quantitative dehydrogenative silylation of phthalimide (product 18),\(^2\) which is a substrate that has previously been shown to be unsuitable for Lewis base catalyzed silylation.\(^2\)

To demonstrate the ability of this approach to selectively generate silyl ethers in the presence of reactive C–H bonds, we performed the dehydrosilylation of 3-ethynylphenol. Facile hydrosilylation of alkynes has been reported\(^2\)\(^5\)\(^{-2}\), including a report on the base catalyzed hydrosilylation of alkynes.\(^2\)\(^7\) In that recent report, an attempt to selectively silylate alcohols or alkynes led to only doubly silylated product. Our K\(_2\)CO\(_3\)-catalyzed silylation reaction, however, was selective for the dehydrosilylation of alcohol over the hydrosilylation of the alkyne moiety. The previously unreported (3-ethynlphenoxy)triethylsilane product (19) was obtained in 81\% isolated yield, with a minor amount of the doubly silylated product being observed using mass spectrometry.

**Table 2.1:** Potassium carbonate catalyzed silylation of various alcohols with triethyl- or triphenylsilane

<table>
<thead>
<tr>
<th>Product</th>
<th>(\text{OSi(Ph)}_3)</th>
<th>(\text{OSi(Et)}_3)</th>
<th>% Yield</th>
</tr>
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<tbody>
<tr>
<td>10</td>
<td>25</td>
<td>99</td>
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</tr>
<tr>
<td>11</td>
<td>60</td>
<td>98</td>
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<tr>
<td>12</td>
<td>60</td>
<td>99</td>
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<tr>
<td>13</td>
<td>24</td>
<td>94</td>
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</tbody>
</table>
A mechanistic pathway for the base catalyzed dehydrogenative silylation of alcohols has previously been proposed. The mechanism proceeds via the base catalyst interacting with silicon atom to generate a more hydridic hydrosilane. This interaction promotes reactivity with alcohols to produce H₂ and form the Si–O bond. A similar mechanism has been assumed for NaOH catalyzed silylation of alcohols. It is likely that the K₂CO₃ catalyzed silylation reactions in this report operate under a related mechanism, but a detailed mechanism will require future studies. This study has shown, however, that the relatively weak nature of the K₂CO₃ base compared to previous studies has led to exceptional functional group tolerance and operates through dehydrogenative silylation and avoids acidic salt byproducts.

Conclusions

In summary, the K₂CO₃ catalyzed dehydrogenative silylation of a wide variety of alcohols has been achieved. The catalyst is readily commercially available, operates under
mild conditions, and exhibits wide functional group tolerance. Substrates that had previously shown incompatibility with both Lewis acid and base catalyzed reactions were successfully silylated with high yields. The catalyst also exhibited selectivity for hydroxyl groups, allowing for protection chemistry during reactions involving C–H bonds. Overall, the ease of use and breadth of reactivity makes this an appealing approach for the formation of silyl ethers.

Experimental

General Information

All starting materials were obtained from commercial sources and used without further purification. Yields refer to isolated compounds through column chromatography. $^1$H and $^{13}$C NMR spectra were obtained using a Bruker Avance III-HD 300 MHz spectrometer in CDCl$_3$; chemical shifts are reported in parts per million (ppm) relative to chloroform-$d$ (7.27 ppm) for $^1$H NMR. For $^{13}$C NMR, chloroform-$d$ (77.0 ppm, center peak). Multiplicity is indicated using the following abbreviations: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), m (m multipartlet). $^{29}$Si NMR spectra were obtained using a Bruker Avance III-HD 400 MHz spectrometer in CDCl$_3$.

General procedure for the dehydrogenative silylation of alcohols: products 1-19

Reaction vessels were dried under vacuum and the reactions carried out under an inert atmosphere using standard Schlenk line techniques. The silane (1.5 mmol) was added at room temperature to a solution of the alcohol (0.5 mmol) and $\text{K}_2\text{CO}_3$ (20 mol%, 12 mg) in DMF: THF (1:1, 1 mL). After stirring at 25–60 °C for 18 h, the reaction mixture was filtered through celite and the residue was analyzed with GC-MS. Further purification by column chromatography using ethyl acetate:hexane 90:10 solvent mixture gave the isolated
silyl ether product. All products were characterized by the usual spectroscopic techniques or compared with data reported in the literature.

*Spectroscopic results*

**Triethyl(phenoxy)silane (1)** 95% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.20 (t, 2H), 6.94 (t, 1H), 6.86 (d, 2H), 0.99 (t, 9H), 0.74 (q, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 155.60, 129.40, 121.24, 119.98, 6.81, 5.00. Data agrees with literature reports.\(^{29}\)

**Triethyl(2-methylphenoxysilane (2a))** 78% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.06 (d, 1H, $J = 7.4$ Hz), 7.02 (t, 1H, $J = 7.6$ Hz), 6.85 (t, 1H, $J = 7.4$ Hz), 6.76 (d, 1H, $J = 7.6$ Hz), 2.21 (s, 3H), 0.99 (t, 9H, $J = 7.8$ Hz), 0.76 (q, 6H, $J = 7.8$ Hz). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.97, 130.85, 128.80, 126.58, 120.96, 118.40, 16.61, 6.69, 5.33. $^{29}$Si NMR (80 MHz, CDCl$_3$) $\delta$ 19.99. MS: m/z 222 (M+, 63%), 193 (100), 165 (24), 135 (7), 91 (10). HRMS(EI) Calcd for C$_{13}$H$_{22}$OSi (M+): 222.1440; found: 222.1447.

**Triethyl(3-methylphenoxysilane (2b))** 87% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.11 (t, 1H), 6.78–6.65 (m, 3H), 2.31 (s, 3H), 0.99 (t, 9H), 0.77 (q, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 155.54, 139.38, 129.06, 122.05, 120.74, 116.83, 21.40, 6.66, 5.03. Data agrees with literature reports.\(^{30}\)

**Triethyl(4-methylphenoxysilane (2c))** 99% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.01 (d, 2H), 6.74 (d, 2H), 2.27 (s, 3H), 0.97 (t, 9H), 0.69 (q, 6H). $^{13}$C NMR (75MHz, CDCl$_3$) $\delta$ 154.71, 130.41, 129.85, 119.67, 20.57, 6.64, 4.97. Data agrees with literature reports.\(^{29}\)

**Tribromophenoxysilane (3a)** 84% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.52 (d, 1H), 7.13(t, 1H), 6.88-6.78 (m, 2H), 0.99 (t, 9H), 0.78 (q, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 150.27, 133.53, 128.49, 122.37, 120.39, 118.23, 6.80, 5.22. Data agree
with literature reports.\(^\text{31}\)

(3-bromophenoxy)triethylsilane (3b) 91% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.08–7.02 (m, 2H), 7.02 (s, 1H), 6.80–6.76 (m, 1H), 1.00 (t, 9H), 0.71 (q, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 156.52, 130.43, 124.42, 123.36, 122.49, 118.66, 6.81, 4.94. Data agrees with literature reports.\(^\text{32}\)

(4-bromophenoxy)triethylsilane (3c) 99% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.32 (d, 2H), 6.73 (d, 2H), 0.97 (t, 9H), 0.72 (q, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 154.82, 132.31, 121.74, 113.54, 6.81, 4.93. Data agrees with literature reports.\(^\text{33}\)

Triethyl(2-methoxyphenoxy)silane (4a) 87% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.94–6.78 (m, 4H), 3.80 (s, 3H), 0.97 (q, 9H), 0.74 (t, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 151.03, 145.03, 121.68, 120.84, 112.13, 55.48, 6.80, 5.11. Data agrees with literature reports.\(^\text{34}\)

Triethyl(3-methoxyphenoxy)silane (4b) 67% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.11 (t, 1H, \(J = 8.1\) Hz), 6.53–6.42 (m, 3H) 3.77 (s, 3H), 0.98 (q, 9H, \(J = 7.8\) Hz), 0.76 (t, 6H, \(J = 7.8\) Hz). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 160.72, 156.79, 129.69, 112.41, 106.81, 106.16, 55.20, 6.81, 5.01. \(^{29}\)Si NMR (80 MHz, CDCl\(_3\)) \(\delta\) 20.97. MS: \(m/z\) 238 (M+, 60%), 209 (100), 181 (46), 153 (26), 121 (4), 107 (7), 91 (21), 77 (29). HRMS(EI) Calcd for C\(_{13}\)H\(_{22}\)O\(_2\)Si (M+): 238.1389; found: 238.1398.

Triethyl(4-methoxyphenoxy)silane (4c) 99% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.78–6.74 (m, 4H), 3.76 (s, 3H), 0.99 (t, 9H), 0.70 (q, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 154.07, 149.29, 120.50, 114.48, 55.62, 6.63, 4.92. Data agrees with literature reports.\(^\text{29}\)
Triethyl(4-nitrophenoxy)silane (5) 98% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.12–7.02 (m, 2H), 6.91–6.66 (m, 2H), 0.99 (t, 9H), 0.73 (q, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.51, 144.51, 125.97, 121.29, 6.80, 4.42. Data agrees with literature reports.\(^{33}\)

Dimethylphenyl(phenoxy)silane (6) 99% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65–7.62 (m, 2H), 7.42–7.39 (m, 3H), 7.19 (t, 2H), 6.94 (t, 1H), 6.81 (d, 2H), 0.51 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.70, 133.47, 131.16, 130.91, 129.90, 129.25, 128.97, 127.96, 127.71, 120.05, 118.27, 0.86. Data agrees with literature reports.\(^{34}\)

(Phenoxy)triphenylsilane (7) 99% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.68–7.61 (m, 6H), 7.49–7.35 (m, 9H), 7.12 (d, 2H), 6.92–6.85 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 155.21, 135.92, 133.65, 130.51, 129.44, 128.08, 121.65, 120.14. Data agrees with literature reports.\(^{35}\)

Triisopropyl(phenoxy)silane (8) 67% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.23–7.19 (m, 2H), 6.95–6.87 (m, 3H), 1.31–1.26 (m, 3H), 1.21–1.08 (m, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 156.07, 129.34, 120.97, 119.94, 17.92, 12.07. Data agrees with literature reports.\(^{36}\)

Dimethyl tert-butyl(phenoxy)silane (9) 99% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.20–7.18 (m, 2H), 6.94 (t, 1H), 6.83 (d, 2H), 0.98 (s, 9H), 0.19 (s, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 157.18, 129.38, 121.27, 120.12, 30.93, 25.69, -4.42. Data agrees with literature reports.\(^{37}\)

(Benzyloxy)triphenylsilane (10) 99% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.52–7.17 (m, 20H), 4.82 (s, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 135.83, 135.46, 134.01, 130.12, 128.25, 127.93, 127.07, 126.38, 65.58. Data agrees with literature reports.\(^{15}\)
**Triethyl(4-tert-butylbenzylxy)silane (11)** 98% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.39–7.28 (m, 4H), 4.72 (s, 2H), 1.34 (s, 9H), 1.00 (t, 9H), 0.70 (q, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 149.89, 138.28, 126.10, 125.14, 64.54, 34.47, 31.41, 6.81, 4.51. Data agree with literature reports.\(^{38}\)

**{(2-phenylethoxy)triphenylsilane (12)}** 99% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.61–7.12 (m, 20H), 3.93 (t, 2H), 2.81 (t, 2H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 138.82, 135.47, 134.46, 130.14, 129.21, 128.27, 127.95, 126.18, 65.09, 39.25. Data agrees with literature reports.\(^{15}\)

**Triethyl[(3-phenyl-2-propenyl)oxy]silane (13)** 87% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.30–7.21 (m, 5H), 6.60 (d, 1H), 6.36–6.28 (m, 1H), 4.37 (dd, 2H), 1.02 (t, 9H), 0.68 (q, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 137.14, 129.75, 128.50, 127.34, 126.41, 63.60, 6.80, 4.54. Data agrees with literature reports.\(^{39}\)

**{(Cyclohexyloxy)triphenylsilane (14)}** 99% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.52–7.13 (m, 15H), 3.79–3.71 (m, 1H), 1.65–1.03 (m, 5H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 135.48, 135.23, 129.84, 127.87, 127.78, 71.82, 35.61, 25.64, 23.96. Data agrees with literature reports.\(^{15}\)

**{(3-chloropropyl)triethylsilane (15)}** 99% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.77 (q, 2H), 3.68 (q, 2H), 1.94 (m, 2H), 0.97 (t, 9H), 0.66 (q, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 59.84, 40.72, 34.85, 6.78, 4.40. Data agrees with literature reports.\(^{40}\)

**Triethyl(4-methoxypyridyl)silane (16)** 83% yield; colorless oil; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.57 (d, 2H), 7.29 (d, 2H), 4.76 (s, 2H), 1.00 (t, 9H), 0.69 (q, 6H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 150.53, 149.61, 120.68, 63.18, 6.73, 4.42. Data agree with literature reports.\(^{41}\)
Triethyl(furfuryloxy)silane (17) 56% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.38 (d, 1H), 6.31–6.24 (m, 2H), 4.88 (s, 2H), 0.91 (q, 9H), 0.50 (t, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 154.22, 143.65, 110.68, 108.92, 67.81, 6.81, 4.55. Data agree with literature reports.$^{41}$

N(2-((triethylsilyl)oxy)ethyl)phthalimide (18) 99% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.88–7.85 (m, 2H), 7.74–7.71 (m, 2H), 3.86 (s, 4H), 0.91 (t, 9H, $J = 7.9$ Hz), 0.57 (q, 6H, $J = 7.9$ Hz). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 168.33, 133.89, 132.16, 123.17, 59.73, 40.16, 6.60, 4.30. $^{29}$Si NMR (80 MHz, CDCl$_3$) $\delta$ 19.60. MS: $m/z$ 276 (M – Et, 100%), 232 (16), 204 (3), 160 (6), 130 (18), 87 (4). HRMS (EI) Calcd for C$_{16}$H$_{23}$NO$_3$Si (M$^+$): 276.1056; found: 276.1056.

(3-ethynylphenoxy)triethylsilane (19) 81% yield; colorless oil; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.09 (t, 1H, $J = 7.8$ Hz), 6.98 (d, 1H, $J = 7.6$ Hz), 6.87 (s, 1H), 6.71 (m, 1H), 3.05 (s, 1H), 1.00 (t, 9H, $J = 7.8$ Hz), 0.71 (q, 6H, $J = 7.8$ Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.41, 129.42, 125.27, 123.45, 123.05, 121.03, 83.54, 6.59, 4.96. $^{29}$Si NMR (80 MHz, CDCl$_3$) $\delta$ 21.74. MS: $m/z$ 232 (M$^+$, 57%), 203 (100), 175 (49), 147 (42), 115 (5), 101 (22), 88 (18), 74 (17). HRMS (EI) Calcd for C$_{14}$H$_{20}$OSi (M$^+$): 232.1283; found: 232.1293.
References


CHAPTER 3

LOW TEMPERATURE SELECTIVE HYDRODEOXYGENATION OF MODEL LIGNIN MONOMERS FROM A HOMOGENEOUS PALLADIUM CATALYST

Abstract

The molecular, homogeneous catalysts [Pd(tpy)Cl]Cl and [Ni(tpy)](PF$_6$)$_2$, where tpy is 2,2′:6′,2″-terpyridine, have been utilized to perform selective hydrodeoxygenation of benzyl alcohol, benzaldehyde, and benzophenone under very mild conditions. The [Pd(tpy)Cl]Cl catalyst exhibits excellent catalytic activity, with the complete selectivity towards hydrodeoxygenation, even at room temperature. Results indicate that the single-site nature of the molecular catalysts is what leads to the complete selectivity and the absence of aromatic ring hydrogenation products. A two-step mechanism consisting of H$_2$ activation by the catalyst to form a metal hydride complex, followed by selective hydrodeoxygenation is proposed. These results illustrate the possible advantages for the use of homogeneous catalysts in the conversion of lignin biomass to fuel or chemical feedstocks.

Introduction

There has been substantial research carried out within the field of energy in an attempt to find renewable, alternative fuels to replace or supplement conventional fossil fuels.$^1$ Biomass is considered to already be the most cost-effective route to fuels with practical value to produce liquid fuels.$^{2-3}$ The lignocellulose component of biomass is typically comprised of three parts, cellulose (40-50% by weight), hemicellulose (25-35%) and lignin (15-20%).$^4$ The lignin component of lignocellulose is a highly substituted phenolic polymer believed to be formed mainly from three monomeric units; $p$-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.$^5$ However, the catalytic depolymerization of naturally occurring lignin results in a variety of oxygenated products as shown in Figure 3.1. These depolymerization products include, but are not limited to, phenol,$^6-8$ benzyl alcohol,$^8$ benzoic acid,$^9-10$ benzaldehyde,$^9-10$ and various ketones.$^7-9$ The presence of these
oxygenated substituents decreases the energy density of lignin, thus hindering the ability to use lignin effectively as a fuel. The high oxygen content also leads to instability and inherent difficulty to store oxygenates, which represents a major challenge in the ability to use lignin as a renewable chemical feedstock or source of fuel. This provides motivation for research into the upgrading of lignin-derived monomers through the selective removal of oxygenated substituents.

Figure 3.1: General scheme for the synthesis of lignin followed by depolymerization and some commonly formed monomeric units.

The lignocellulose-to-ethanol processes has made use of cellulose and hemicellulose, however leaves the lignin component behind as waste. Typically, lignin is utilized as a low-grade energy source through combustion without further upgrading the energy content. However, the chemical structure of lignin displays potential to be used as a viable chemical feedstock through depolymerization to monomeric units. The upgrading of lignin to fuel requires the deoxygenation of the monomeric units following the depolymerization process. Selective deoxygenation of monomeric units from lignin will not only increase energy density of the monomers, but could also lead to the development of new chemical feedstocks. Hence, removal of oxygen content is required to upgrade lignin to produce petroleum-like hydrocarbons through a selective hydrodeoxygenation process. This removal of oxygen can be examined more closely through the use of compounds that model the monomeric units of lignin. Aromatic compounds possessing alcohols or other oxygenated substituents are widely available, thus
allowing the testing of selective hydrodeoxygenation. The model compounds chosen for this study, benzyl alcohol, benzaldehyde, and benzophenone, contain three of the common structural motifs found in depolymerized lignin.

The upgrading of lignin through hydrodeoxygenation is generally carried out through the use of heterogeneous catalytic systems which operate at high temperatures and pressures. Many studies have explored the use of traditional sulfide catalysts that are typically employed in the petroleum industry for hydrodesulfurization, notably supported catalysts of nickel, platinum, and palladium as well as bimetallic systems of molybdenum with either nickel or cobalt. Catalytic activity of these heterogeneous catalysts, however, tends to not produce selective hydrogenolysis of the C–O bonds and often times leads to hydrogenation of the aromatic rings while leaving behind the targeted oxygenated substituents. Selective deoxygenation of benzaldehyde and benzyl alcohol has been achieved via electrochemical and photochemical methods. The lack of selectivity and the use of high energy inputs led us to pursue single-site homogeneous catalytic systems that have the ability to selectively hydrodeoxygenate monomers derived from lignin.

Single-site molecular catalysts have previously been studied for the deoxygenation of organic compounds. Additionally, the activation of C–O bonds in aryl compounds has also been investigated through the use of homogeneous systems. In an effort to upgrade lignin-derived monomers, a specific understanding of C–O bond activation through the use of homogeneous catalysts is required. Through the use of single-site molecular catalysts, the ability to selectively perform deoxygenation reactions without exhausting energy and catalysts on hydrogenation of the aromatic rings in phenolic monomers is feasible. Polypyridyl complexes of Ni and Pd, specifically Ni and Pd
complexes of 2,2′:6′,2″-terpyridine (tpy) have displayed the ability to activate C–X bonds, where X = O, halogen, S and N.²⁹

![Figure 3.2: Structure of metal-terpyridine catalysts. M = Ni, Pd](image)

The chemical structure of the homogeneous catalysts utilized in this work can be found in Figure 3.2. Nickel and palladium centered catalysts were chosen due to previously reported activity towards C–heteroatom bonds. The tpy ligand was chosen due to the strong σ-donation of the ligand generating an electron-rich metal center, while simultaneously tpy is a π-acceptor, which helps lower the energy required for the chemical reduction of the metal complex. In addition, the chelate effect from the multiple N-binding sites generates a structurally stable catalyst. The increased stability of the catalyst allows for the use of elevated temperatures and pressures, while maintaining structural integrity and hence catalytic activity.

In this work, the selective hydrodeoxygenation of model compounds of lignin was investigated under relatively mild conditions (T = 25 °C – 200 °C, P = 10 – 20 bar H₂). The reactivity of analogous Ni and Pd based catalysts are compared. The molecular, homogeneous Pd-tpy catalysts exhibited excellent selectivity towards the hydrodeoxygenation of benzylic oxygenates. These results indicate that catalysis operates
through two consecutive steps, which are the activation of an H₂ molecule, followed by selective hydrodeoxygenation of the model substrates.

**Results and discussion**

Batch reactions with constant stirring were carried out per the outline seen in Figure 3.3. In this work, benzyl alcohol, benzaldehyde, and benzophenone have been used as model compounds for monomeric units derived from lignin. Work has been done to show that the reactivities of allylic and benzylic alcohols are similar in nature. Both substrate and catalyst exhibited solubility in methanol and methanol is commonly used as a solvent for depolymerization of lignin. Catalyst loadings were maintained a 5 mol% with respect to the substrates, with substrate loading at 0.1M in 50 mL of solvent.

**Figure 3.3:** General scheme for hydrodeoxygenation reactions

The results of an initial screening of the catalysts, and catalytic system, is shown in Table 3.1. Under mild conditions of just 100 °C and 20 bar H₂, the palladium-tpy catalyst converted >99% of the benzyl alcohol with complete selectivity to the desired toluene product as confirmed by gas chromatography-mass spectroscopy (GC-MS). Hydrogenation of the aromatic ring to form cyclohexane, a common product in many heterogeneous catalytic hydrodeoxygenation reactions, was not observed. This selectivity
towards hydrodeoxygenation over hydrogenation illustrates an advantage of homogenous catalytic systems. As can also be noted in Table 3.1, at 100 °C the nickel-tpy catalyst did not exhibit any activity towards benzyl alcohol. Raising the temperature to 200 °C did result in a 5% conversion of benzyl alcohol, however, the major product of that reaction was the undesired 1-methoxymethyl benzene. Similar products have been formed through a Lewis acid etherification process.31-32

**Table 3.1:** Examination of catalytic system for selective hydrodeoxygenation of benzyl alcohol

<table>
<thead>
<tr>
<th>Catalysta</th>
<th>H₂ (bar)</th>
<th>Temp (°C)</th>
<th>Rxn. (bar)b</th>
<th>Convers. (%)c</th>
<th>Select. (%)d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-tpy</td>
<td>20</td>
<td>100</td>
<td>27</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Ni-tpy</td>
<td>20</td>
<td>100</td>
<td>27</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ni-tpy</td>
<td>20</td>
<td>200</td>
<td>58</td>
<td>&lt;5</td>
<td>28</td>
</tr>
<tr>
<td>Pd-tpy</td>
<td>0</td>
<td>100</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>None</td>
<td>20</td>
<td>25</td>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

a5 mol% catalyst in 50 mL of methanol. Reaction time 24 hrs. btotal pressure after heating reaction. cPercent conversion of benzyl alcohol. dPercent selectivity for toluene product.

Control reactions showed that no conversion of the benzyl alcohol substrate was observed with complete removal of the catalyst or in the absence of H₂. In addition, Table 3.2, shows that conversion of benzyl alcohol to toluene increases with an increasing amount of H₂ at room temperature. This increase occurs despite the fact that H₂ is in ten-fold excess of catalyst at 10 bar H₂ and room temperature.33 These results indicate that the catalyst needs to first activate H₂, forming a metal-hydride, before reacting with the benzyl alcohol substrate as illustrated in Figure 3.4. This proposed mechanism can also account for the poor activity of the Ni-tpy catalyst compared to the Pd-tpy catalyst as Pd is known to more efficiently activate H₂ in comparison to Ni.34
Reactions were performed under a variety of conditions to gain a further understanding of the reactivity of the Pd-tpy catalyst. A summary of those reactions is shown in Table 3.2. Under all conditions the Pd-tpy catalyst exhibited complete selectivity towards toluene production from benzyl alcohol. Reactions performed at room temperature remarkably lead to the conversion of benzyl alcohol while maintaining selectivity for the formation of toluene. The reactions were also sensitive to hydrogen pressure as conversion of benzyl alcohol dropped from 42% to 11% when the pressure of \( \text{H}_2 \) was decreased from 20 bar to 10 bar at room temperature. This dependence occurs even with a 10-fold excess of hydrogen with relation to the catalyst at 10 bar \( \text{H}_2 \) at room temperature.\(^{33} \) This dependence of hydrogen pressure on conversion at lower temperatures while maintaining selectivity indicates that a slight elevation in temperature is required for efficient \( \text{H}_2 \) activation by the Pd-tpy catalyst (step 1 Figure 3.4). The \( \text{H}_2 \) dependence in the excess of \( \text{H}_2 \) also indicates that activation of \( \text{H}_2 \) is the rate determining step and once the metal-hydride complex is formed the selective hydrodeoxygenation of benzyl alcohol (step 2 Figure 3.4) is facile in comparison.\(^ {24} \)
Table 3.2: Summary of the selective catalytic deoxygenation of benzyl alcohol from Pd-tpy

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$H_2$ (bar)</th>
<th>Temp (°C)</th>
<th>Rxn. P (bar)$^b$</th>
<th>Convers. (%)$^c$</th>
<th>Select. (%)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>25</td>
<td>10</td>
<td>11</td>
<td>&gt;99</td>
<td>&gt;99</td>
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<tr>
<td>20</td>
<td>25</td>
<td>20</td>
<td>42</td>
<td>&gt;99</td>
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<tr>
<td>10</td>
<td>100</td>
<td>15</td>
<td>61</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>27</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

$^a$5 mol% catalyst in 50 ml of methanol. Reaction time 24 hrs. $^b$Total pressure after heating reaction. $^c$Percent conversion of benzyl alcohol. $^d$Percent selectivity for toluene product.

The results from Table 3.2 led us to examine further substrates pertinent to lignin monomer deoxygenation and to optimize reaction times. Table 3.3 summarizes the results of the hydrodeoxygenation studies for benzyl alcohol, benzaldehyde, and benzophenone. As can be seen, all of the oxygenated motifs were selectively hydrodeoxygenated under mild conditions. It was determined that it required only 4 hours to almost quantitatively convert the substrates. Under the conditions listed in Table 3.3, the turnover frequencies of the reactions are $5.0 \text{ hr}^{-1}$ for benzyl alcohol and benzaldehyde, and $4.8 \text{ hr}^{-1}$ for benzophenone. These turnover frequencies are comparable to previously reported catalytic hydrodeoxygenation reactions.$^{24}$

Table 3.3: Summary of catalytic hydrodeoxygenation reactions

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Substrate$^b$</th>
<th>$H_2$ (bar)</th>
<th>Temp (°C)</th>
<th>Rxn. P (bar)$^c$</th>
<th>Convers. (%)</th>
<th>Select. (%)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzyl Alcohol</td>
<td>20</td>
<td>100</td>
<td>27</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>Toluene</td>
</tr>
<tr>
<td></td>
<td>Benzaldehyde</td>
<td>20</td>
<td>100</td>
<td>27</td>
<td>96</td>
<td>&gt;99</td>
<td>Toluene</td>
</tr>
<tr>
<td></td>
<td>Benzophenone</td>
<td>20</td>
<td>100</td>
<td>27</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>Diphenyl Methane</td>
</tr>
</tbody>
</table>
Complete selectivity for the formation of hydrodeoxygenation products from benzophenone, benzaldehyde, and benzyl alcohol under a wide range of percent conversions (11% – >99%) illustrates the inherent selectivity of the homogeneous Pd-tpy catalyst towards hydrodeoxygenation. Under our standard reaction conditions (20 bar H$_2$, 100 °C, 5 mol% catalyst), no aromatic ring hydrogenation products were formed. In addition, no catalyst degradation was observed and there was no evidence for the formation of Pd or Ni nanoparticles. A reaction performed with ≥1.0 nm Pd particles on mesoporous silica SBA-15 support, as shown in Table 3, resulted in complete conversion of benzyl alcohol, however selectivity towards the deoxygenated product decreased to 56%. The other major product detected by GC-MS was complete hydrogenation to form methylcyclohexane with a 23 % yield. The identity of the remaining 21% was not identified. This result further illustrates the difference between the homogeneous catalyst and heterogeneous catalysts under similar conditions.

Furthermore, conditions were discovered that lead to homogeneous catalyst degradation and the formation of ring hydrogenated products. The base potassium tert-butoxide had previously been shown to increase reactivity with Ni catalysts towards the selective cleavage of C–O bonds in arenols or aryl ethers.$^{28}$ The addition of potassium tert-butoxide to a reaction containing 5 mol% Pd-tpy catalyst at 100 °C, however, resulted in a variety of hydrogenated products including methylcyclohexane, but with 0% selectivity towards the hydrodeoxygenated toluene product. After the reaction, the solution was absent.
of the homogeneous catalyst and contained solid black particles. These particles were not characterized but are likely metallic Pd particles.

**Conclusions**

This study shows an example of highly selective homogenous hydrodeoxygenation of motifs commonly found as products during the catalytic depolymerization of lignin. Under mild conditions, including room temperature and 10 bar H\(_2\) pressure, the Pd-tpy catalyst is able to selectively hydrodeoxygenate benzyl alcohol, benzaldehyde and benzophenone. The key component of this process is the selectivity of the hydrodeoxygenation process without the hydrogenation of the aromatic ring, therefore conserving energy, catalyst, and chemical feedstock. The lack of hydrogenated products further supports that there is no catalyst decomposition during the process of the reaction as the selectivity is achieved by the homogeneous nature of the catalyst. This study illustrates the possible advantages of the utilization of homogeneous catalysts in biomass conversion catalysis.

**Experimental**

*Materials and Instrumentation*

Methanol (MeOH) (99.8%, VWR) was used as the solvent for all catalysis reactions. K\(_2\)PdCl\(_4\) (99.99% trace metals basis, Beantown Chemical), 2,2':6',2''-terpyridine(tpy) (97%, Alfa Aesar) and benzyl alcohol, benzaldehyde, and benzophenone were purchased and used without any further purification. Hydrogen (H\(_2\)) (>99.95%, Praxair) was used during catalysis experiments. Gas chromatography was performed on a HP-5890 GC (Agilent). The separation column was a 30-meter-long Rtx-5 (Restek) with a 0.25 mm id and the oven temperature program was 50°C for 3 minutes followed by a 10°C/min ramp to 300°C. Mass spectrometer was a VG70S magnetic sector instrument.
(Waters). Electron ionization was at 70 eV and the spectrometer was scanned from 450 to 50 m/z at low resolution. $^1$H NMR spectroscopy was performed using Bruker Advance III HD 300. NMR data were processed by Bruker’s TopSpin software. Reference DMSO peak for $^1$H NMR was defined as 2.50 ppm.

**Synthesis**

$\left[(2,2':6',2''\text{-terpyridine})\text{PdCl}\right]\text{Cl}$ was synthesized via an adapted procedure from Yilmaz.$^{35}$ $\text{K}_2\text{PdCl}_4$ (360 mg, 1.1 mmol) was suspended in 25 mL of ethanol (EtOH) and heated to reflux. 257 mg (1.1 mmol) of 2,2':6',2''-terpyridine dissolved in 15 mL of ethanol was added dropwise to the refluxing solution. The reaction mixture became less cloudy with the addition of terpyridine and was further refluxed for 3 hours. A white precipitate formed through the course of the reflux. The resulting solution was cooled and filtered to remove KCl. Solvent was removed via rotary evaporation to yield an orange-brown solid. Yield: 335 mg (0.81 mmol, 74%). $^1$H NMR (DMSO-$d_6$, ppm): 8.792 (d, 2H), 8.657 (d, 2H), 8.643 (d, 1H), 8.503 (t, 3H), 7.940 (t, 2H).

$\left[(2,2':6',2''\text{-terpyridine})\text{Ni}\right]\text{(PF}_6\text{)}_2$ was synthesized according to literature procedure.$^{36}$

Palladium nanoparticles supported on mesoporous silica, Pd/SBA-15 was prepared by the method of strong electrostatic adsorption with synthesis conditions based on prior work.$^{37}$ SBA-15 support (SA = 1270 m$^2$/g) was added to an aqueous solution of Tetraamminepalladium(II) chloride, Pd(NH$_3$)$_4$Cl$_2$. The palladium solution pH was initially adjusted with ammonia solution to pH 10.8 before adding the support. The amount of silica added was controlled to achieve a slurry surface loading of 1000 m$^2$ surface per liter of solution. The slurry was placed in an HDPE bottle and agitated on an orbital shaker for an hour at a rate of 120 rpm. After contact time, the pH of the slurry was measured to be 10.4.
The slurry was vacuum filtered with the solids collected and dried at 120 °C overnight. The initial and final Pd concentration (14.2 ppm and 3.46 ppm respectively) was measured using ICP-OES and the loading of the Pd on the catalyst powder was calculated to be 1.3 wt% Pd/SBA-15.

To generate the nanoparticles, the dried powder was then subjected to thermal treatment in a horizontal tube furnace with reduction done by ramping at 1°C/min to 200°C, in 20% hydrogen with helium as balance of the gas flow of 250 sccm. The resulting catalyst powder was characterized by X-ray diffraction to determine formation of Pd nanoparticles. The XRD patterns for the support and final catalyst give a particle size estimation of very small particles equal to or less than 1 nm. This value is in accordance with the detection limits of the XRD instrument shown in previous work.38

*General Reaction Procedure*

All reactions were performed in a 130-mL capacity batch reactor. For a typical experiment, 520 μL (0.10M) of benzyl alcohol, 100 mg (5.0 mol%) of [Pd(tpy)Cl]Cl, were mixed in 50 mL methanol. The catalytic solution was then sealed in the batch reactor and purged with 25 bar H2 at least 5 times. Then, the reactor was filled with the desired pressure of H2 and sealed for the duration of the experiment. The batch reactor was then heated through the use of a heating jacket to the desired temperatures. The reaction was stirred for the duration of the catalytic experiment, 24 hours. The products were then analyzed through GC-MS following filtration through a silica plug to remove the catalyst.
References


CHAPTER 4

A SILICA SUPPORTED MOLECULAR PALLADIUM CATALYST FOR SELECTIVE HYDRODEOXYGENATION OF AROMATIC COMPOUNDS UNDER MILD CONDITIONS

Adapted with permission from DeLucia, Nicholas A.; Jystad, Amy; Vander Laan, Katherine; Tengco, John Meynard M.; Karakalos, Stavros G.; Caricato, Marco; Vannucci, Aaron K.; under rev. ACS Catal.
Abstract

The molecular complexes, chloro(2,2′:6′,2′′-terpyridine-4′-carboxylic acid)palladium(II) chloride and chloro([-[(2,2′:6′,2′′-terpyridin)-4′-yl] benzoic acid)palladium(II) chloride, were synthesized and used to modify the surface of amorphous silicon dioxide to generate a hybrid molecular/heterogeneous catalyst. This hybrid catalytic system exhibited excellent selectivity (>90%) for hydrodeoxygenation of oxygenated aromatics under mild reaction conditions. Spectroscopic techniques such as XPS, XRD and solid-state NMR, in conjunction with ICP-MS, indicate that the molecular catalyst is present on the surface of SiO₂ and the formation of unwanted metallic Pd nanoparticles can be avoided. Computational modeling shows the complexes can “bind” to the oxide surface through a hydrogen bonding interaction or via a Coulombic attraction between the charged molecule and the oxide surface. Post reaction analysis of the surface-modified oxide catalysts confirmed prolonged molecular integrity of the catalysts and sustained binding of the catalysts to the oxide surface when nonpolar solvents were employed for reactions. These surface-attached molecular catalysts thus were easily recycled through multiple catalytic reactions.

Introduction

Biomass is the largest possible renewable carbon source available. Composed of cellulose, hemicellulose, and lignin, lignocellulosic biomass is also highly oxygenated.¹ The cellulosic component of biomass is both an agricultural feedstock, and an industrially relevant source of renewable fuel additives.² Lignin, however, is both not an edible component of biomass and is typically treated as waste and burned for energy during cellulose processing.³ Yet, obtaining higher value from lignin, such as deriving chemical feedstocks and fuel, is being recognized as integral to the economic feasibility of
biorefineries. Lignin is a polymer containing aromatic subunits, thus, could be a viable source for commodity chemicals and liquid fuels. Upgrading lignin to fuel first requires the depolymerization of lignin to form oxygenated aromatic monomers. Recent advances, such as “lignin first” processes have greatly increased the efficiency of lignin depolymerization. Deoxygenation of the aromatic units would increase the energy density of the resulting liquid fuel, or lead to the isolation of important industrial chemical feedstocks. Selectively deoxygenating lignin derived compounds without hydrogenation of the aromatic units is of specific interest because it would remove oxygen as water, maximize the hydrogen use efficiency, minimize carbon loss which prevents char and catalyst deactivation, and aromatics and alkenes are higher value chemicals compared to alkanes.

Numerous catalytic studies have examined the selective deoxygenation of aromatic units. Partial deoxygenation of lignin derived monomers has been shown to occur during catalytic depolymerization studies. Though, many studies have focused on the deoxygenation of model substrates to examine the efficiency of deoxygenation catalysts. The vast majority of the research involved in catalytic deoxygenation employs the use of metal nanoparticle, heterogeneous catalytic systems. Addition of Zn to the reaction solution containing Pd nanoparticles on a carbon support has been shown to increase the selective deoxygenation of the benzylic position of vanillyl alcohol. Controlling the hydrophilicity of the catalyst support and surface can also increase the catalytic efficiency of vanillyl alcohol deoxygenation. Ru/Nb particles supported on SiO2 have shown the ability to catalytically convert p-cresol to toluene with selectivities as high as 85%. Direct deoxygenation of guaiacol to benzene and p-cresol to toluene with good selectivities have also been observed for various nanoparticle catalysts. Carbon coated Pt(111)
samples or rutile TiO$_2$ (110), when properly prepared, exhibited great selectivities for the deoxygenation of benzyl alcohol to toluene. This selectivity is further impressive since it is proposed that the extended surfaces of nanoparticle catalysts is what leads to ring hydrogenation of oxygenated aromatics.$^{18}$ In fact, atomically dispersed cobalt on MoS$_2$ nanomaterials was recently able to achieve selective deoxygenation of phenolics without observed ring hydrogenation.$^{19}$

Another approach to avoiding ring hydrogenation and extended catalyst surfaces is through the use of molecular catalysts. Molecular catalysts can be highly selective, and product selectivity can be tuned through well-known synthetic modifications of the catalyst structure.$^{20-21}$ Activities of molecular catalysts also tend to be high.$^{22-23}$ Utilizing molecular catalysts in large scale industrial reactions, however, is commonly limited by the robustness of the catalysts and the difficulty of post reaction separations of a homogeneous catalyst solution. Conversely, heterogeneous catalysts are commonly employed in large scale industrial settings, such as steam reforming and hydrocarbon cracking, due to the ease of separation and robustness of the catalysts.$^{24-25}$ Heterogeneous catalysts, however, tend to lack product selectivity when compared to homogenous catalysts.$^{26-27}$ Combining the positive aspects of homogeneous selectivity and heterogeneous robustness and ease of post reaction separations could lead to the development of ideal catalysts for selective deoxygenation reactions.

The use of homogeneous catalysts for the deoxygenation of organic compounds has been explored, as well as probing the activation of C–O bonds in homogeneous systems.$^{28-32}$ Recently, we have reported the homogeneous molecular (2,2′:6′,2″-terpyridine)palladium(II) catalyst is capable of low temperature, selective HDO of model lignin monomers, specifically benzylic substrates.$^{33}$ The catalyst showed complete
selectivity for deoxygenated products over ring hydrogenated products, with high conversions at 100 °C. Catalyst recyclability was difficult due to the need to separate the homogeneous catalyst from the reaction mixture through column chromatography. To increase the recyclability of our catalytic system, we have synthetically modified the 2,2′:6′,2″-terpyridine ligand in order to attach the catalyst to a SiO₂ support. The molecular catalysts utilized for this study is shown in Figure 4.1 along with a representation of the molecular catalyst modified SiO₂ supports.

**Figure 4.1:** Structures of chloro(2,2′:6′,2″-terpyridine-4′-carboxylic acid)palladium(II) chloride (1), chloro(−[(2,2′:6′,2″-terpyridin]-4′-yl) benzoic acid) palladium(II) chloride (2), and a graphical representation of the molecular catalysts attached to a SiO₂ supports (1-SiO₂ and 2-SiO₂).

Research in the field of surface modified metal oxide supports with molecular catalysts has been most thoroughly studied with dye-sensitized solar cells (DSSCs), dye-sensitized photoelectrosynthesis cells (DSPECs), and electrochemical oxidations. The general approach for modifying oxide surfaces with molecular catalysts is through “binding
groups”. These binding groups are typically acid functionalities, such as carboxylate, phosphonate, and hydroxymate, covalently bound to polypyridyl ligands. Synthetic methods for the preparation of polypyridyl ligands containing binding groups are readily available. The binding-group-polypyridyl-ligand unit then bonds to transition metals to generate molecular catalysts that can be attached to the surface of metal oxide particles. This attachment generates a hybrid heterogeneous catalyst with the activity and selectivity of a homogeneous molecular catalyst. A wide variety of metal oxide particles are amenable to this binding motif including SiO\(_2\), TiO\(_2\), tin-doped indium oxide, and fluoride-doped tin oxide, however, the exact nature and energetics of this binding interacting is still not well known. However, multiple reports have qualitatively shown that this binding motif is stable under a variety of conditions, and that molecular catalysts can remain bound to oxide surfaces for extended periods of time.

A large amount of work has been dedicated to the study of metal oxides modified with molecular catalysts for the photo- and electro-chemical applications mentioned above, however, thermally activated catalytic processes have also been explored with this catalytic motif. While multiple successes have been reported, a critical review examined the stability of these molecular-heterogeneous catalysts. The review concluded that many of the catalysts on oxide supports decomposed into homogeneous catalysts and thus extensive characterization of these catalytic systems is necessary to confirm the nature of the catalysts. The main decomposition route for Pd-based catalysts was through a Pd leaching from the chosen ligand and not from detachment of the binding group from the surface of the metal oxide. The authors of the review suggested many tests to confirm whether a catalyst is truly heterogeneous, and these tests include recycling the heterogeneous
catalysts, extensive characterization post reaction of the metal oxide supports, and testing for catalytic activity in solutions that have been exposed to the heterogeneous catalysts.

Many thermally activated catalytic processes have not been explored using this catalytic motif of molecular catalysts attached to the surface of metal oxides. This lack of exploration is due to concern for molecular decomposition of the catalysts at elevated temperatures. However, a common route for molecular catalyst decomposition is through a bimolecular pathway, and it has been shown that the immobilization of molecular catalysts prevents bimolecular decomposition pathways. Thus, solid supported molecular catalysts should be explored as a promising route for thermally activated catalytic pathways.

A specific example of a thermally activated catalytic route that should be amenable to molecular catalysts is the conversion of biomass to liquid fuels through hydrodeoxygenation. The lignocellulose component of biomass is composed of roughly 20% lignin by weight, with the remaining weight being composed of cellulose and hemicellulose. The conversion of lignocellulose to ethanol is already a widely used catalytic transformation, but this process leaves the lignin component as waste. These depolymerization products include, but are not limited to, phenolic units, benzyl alcohol, benzoic acid, benzaldehyde, and various ketones. To convert these monomeric units to higher energy density fuel that is easily stored, selective deoxygenation of the monomer units is necessary. The need for the selective deoxygenation of the lignin monomers makes the high selectivity of molecular catalysts a favorable target for this chemical transformation.

In this work, 1-SiO₂ and 2-SiO₂ were examined for the selective HDO of oxygenated aromatics under a variety of catalytic conditions. Using a solid metal oxide
surface-modified with a molecular catalyst introduces a new catalytic motif to the field of catalytic hydrodeoxygenation. This hybrid molecular/heterogeneous catalyst motif has been characterized both pre- and post-reaction to show the molecular catalysts is attached to the oxide support and remains attached throughout multiple catalytic cycles. Furthermore, computational modeling has been used to explore and quantitate the possible geometries and binding energies between the carboxylate binding groups and the SiO₂ support.

Results and discussion

Catalyst Preparation

The synthesis of the molecular catalysts 1 and 2 and their attachment to SiO₂ to generate 1-SiO₂ and 2-SiO₂, was supported by a variety of characteristic techniques. Following a soaking period of the A300 SiO₂ particles in a 1.0 mM solution of 1 or 2, the particles were filtered and rinsed with cold methanol. The resulting oxide solid was no longer white, but instead colored, indicative of the molecular complexes 1 (yellow) and 2 (red-orange). To determine the amount of palladium present in a sample of 1-SiO₂, 0.01g of the solid catalyst was digested with 4 mL aqua regia at 180°C (heat block) for 5 hours. The digestate was brought to ~10g before ICP-MS analysis. ICP-MS analysis showed that 1-SiO₂ contained 2.1 wt.% Pd. This equates to 6.6x10⁻⁷ mol of catalyst per m² of silica support. To determine the surface coverage of the molecular catalysts on the surface of A300 – the spatial area of the catalyst in two different orientations was estimated from van der Waal radii and bond lengths. Figure 4.2 illustrates an aerial view of 1-SiO₂ in two possible orientations: “standing” perpendicular to the surface of the SiO₂ and “laying” parallel to the surface. As can be seen in Figure 4.2, the laying configuration of the complex would cover an area approximately 4 times that of the standing configuration. If all of the molecular complexes
were in the laying configuration and given the amount of Pd determined through ICP-MS, the surface coverage would be much greater than one monolayer of catalyst. Achieving greater than one monolayer of surface coverage is unlikely due to a lack of attractive forces to stabilize a multilayer structure. In addition, multilayers have not been reported for similar catalyst motifs. Conversely, if the area of the catalyst in the standing configuration is used, it is estimated that approximately all of the surface if covered by catalyst. This suggests that 1-SiO$_2$ and 2-SiO$_2$ likely are in the standing configuration, near perpendicular to the surface of the SiO$_2$ support, though there is a possibility of multiple orientations being present simultaneously.

![Diagram of catalyst orientations](image)

\[ A = 4.7 \times 10^5 \text{ pm}^2 \quad A = 1.6 \times 10^6 \text{ pm}^2 \]

**Figure 4.2**: An aerial view of 1-SiO$_2$ in perpendicular (left) and parallel (right) orientations on surface of silica. A = area.

The preparations of 1-SiO$_2$ and 2-SiO$_2$ are direct and does not expose the catalyst to any increase in temperature or reductive/oxidative conditions, thus it is reasonable to assume all the palladium detected using ICP-MS is present in the molecular catalyst form shown as 1-SiO$_2$ and 2-SiO$_2$ in Figure 4.1. To support this assumption, we further characterized the catalyst using solid-state NMR and powder XRD. Evidence for the tpy ligand being attached to the SiO$_2$ surface can be seen via solid-state $^{13}$C NMR, in which
peaks corresponding to the 2,2′:6′,2″-terpyridine-4′-carboxylic acid ligand can be observed (Figure 3.3). The large peaks observed in the NMR spectra in Figure 4.3 (161.61, 34.61 and 29.45) correspond to DMF solvent, which was the used to prepare 1-SiO₂ and was still present adsorbed to the surface of the silica particles. Solid-state NMR was not performed on 2-SiO₂ due to this catalyst’s inferior performance in relation to 1-SiO₂, which will be discussed later in this chapter.

Figure 4.3: ¹³C NMR spectra of 1-SiO₂ as prepared

X-ray diffraction patterns of 1-SiO₂ and 2-SiO₂ on A300, compared with fresh A300, showed no presence of metallic palladium in either of the samples (Figure 4.4), noting that the detection limit of the XRD instrument used is 1.5 nm crystalline particles.⁵⁶⁻⁵⁷ The determination that there is no presence of metallic palladium in the two catalyst samples was to be expected, as the catalysts were not exposed to conditions that would
suggest the decomposition of 1 or 2. Combining the measured concentration of palladium as detected by ICP-MS, along with the solid-state NMR and XRD results, the case is strong for surface-attached molecular catalysts on A300 support.

![Graph showing powder X-ray diffraction profiles](image)

**Figure 4.4**: Powder X-ray diffraction profiles of fresh Aerosil300 (red), prepared 1-SiO$_2$ (blue) and prepared 2-SiO$_2$ (green)

**Catalytic Testing**

With the success of derivatizing the surface of A300 with molecular catalysts 1 and 2, batch reactions in methanol were carried out to test the catalytic activity of 1-SiO$_2$ and 2-SiO$_2$ towards the selective hydrodeoxygenation of benzyl alcohol. This model substrate and solvent were chosen for a direct comparison to previously reported homogenous catalysis results. In that previous report, homogeneous catalyst chloro(2,2':6',2'''-terpyridine)palladium(II) chloride was able to convert benzyl alcohol to toluene with complete selectivity at 100 °C at an average turn over frequency of 5.0 hr$^{-1}$ over the course of 4 hours. Table 4.1 lists the catalytic results for the HDO of benzyl alcohol using various heterogeneous catalysts. The hybrid molecular/heterogeneous catalysts 1-SiO$_2$ and 2-SiO$_2$
did perform selective HDO of benzyl alcohol to toluene at room temperature, though low conversions (< 10 %) were observed over the course of 4 hours. When the temperature of the reaction was increased to 100 °C, benzyl alcohol conversion increased while selectivity to the desired toluene product was maintained. The average turnover frequency for this catalytic transformation in methanol was 2.5 hr⁻¹ over the course of 4 hours. No conversion of the benzyl alcohol substrate was observed without the surface-attached molecular catalyst (just SiO₂), without hydrogen gas, or with a complete lack of all catalyst components. Pre-made Pd nanoparticles on SBA-15 (discussed in the experimental section) were also tested for comparison. As can be seen in Table 3.4, the Pd nanoparticles were more active for benzyl alcohol conversion, however, the particles were not nearly as selective towards the desired HDO product and instead formed a considerable amount of ring hydrogenated products. This illustrates the clear catalytic advantage of molecular catalyst being attached to oxide support compared to general nanoparticle catalysts.

Table 4.1: Examination of catalytic performance for the selective HDO of benzyl alcohol to toluene.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>H₂ (bar)</th>
<th>Temp. (°C)</th>
<th>Rxn P (bar)</th>
<th>Convers. (%)</th>
<th>Select. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-SiO₂ᵃ</td>
<td>20</td>
<td>25</td>
<td>20</td>
<td>8</td>
<td>&gt;99</td>
</tr>
<tr>
<td>1-SiO₂ᵃ</td>
<td>20</td>
<td>100</td>
<td>27</td>
<td>35</td>
<td>&gt;99</td>
</tr>
<tr>
<td>Just SiO₂</td>
<td>20</td>
<td>100</td>
<td>27</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>None</td>
<td>20</td>
<td>100</td>
<td>27</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1-SiO₂</td>
<td>0</td>
<td>100</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Pd particlesᵉ</td>
<td>20</td>
<td>100</td>
<td>27</td>
<td>&gt;99</td>
<td>56ᶠ</td>
</tr>
</tbody>
</table>

ᵃ8.8x10⁻⁵ mol 1 (450 mg total 1-SiO₂) in 25 mL of methanol with 0.1 M benzyl alcohol. Reaction time 4 hrs.
ᵇTotal pressure inside the reactor during reaction.
Percent conversion of benzyl alcohol.
Percent selectivity for toluene formation.
>1.0 nm Pd particles prepared on SBA-15.
Other major product detected was methyl cyclohexane in 23 % yield.

As 1-SiO₂ exhibited greater % conversion of benzyl alcohol to toluene, this catalyst was chosen for further optimization. Before moving on, the spent 1-SiO₂ following both room temperature and 100 °C reactions was characterized with powder XRD to determine whether or not the catalyst is being reduced during the course of a reaction. The powder XRD profiles seen in Figure 4.5 show that the catalyst does indeed reduce to metallic Pd nanoparticles following a 100 °C reaction in methanol, while there are no observed particles at room temperature. While the catalyst was active for the selective HDO of benzyl alcohol, conversions were very low while using methanol as the solvent.

Figure 4.5: Powder X-ray diffraction profiles of 1-SiO₂ following a reaction at room temperature (blue) and 100 °C (green) in methanol. Metallic Pd peak positions denoted with a diamond.
To further optimize the catalytic performance, various solvents were explored. Solvents such as acetic acid and water were chosen to complement work that has performed in lignin depolymerization studies. Additionally, dodecane was chosen as a nonpolar solvent for comparison to the polar solvents selected. The catalytic testing of 1-SiO$_2$ in the chosen solvents is shown in Table 4.2. Little reactivity was observed in water at room temperature and 100°C. This lack of reactivity can be rationalized by highly polar water both detaching the catalyst off the metal oxide support and decomposing the molecular catalyst to a Pd-aqua complex. Similarly, using acetic acid as a solvent at room temperature yielded very little benzyl alcohol conversion. However, the 100°C reaction of 1-SiO$_2$ in acetic acid led to complete conversion of benzyl alcohol. The increase in conversion was concurrent with a decrease in selectivity for the HDO product toluene as benzyl acetate was also observed in the product solution. Switching from polar solvents to non-polar dodecane provided both an increased conversion of benzyl alcohol and complete selectivity to the desired HDO product. Dodecane may be an ideal solvent for this catalytic system as the non-polar nature of the solvent may stabilize catalyst binding to the oxide support. Dodecane should not hydrogen bond to the oxide surface, and the charged molecular, catalyst 1 has poor solubility in dodecane. At room temperature in dodecane solvent, 1-SiO$_2$ was able to achieve 61% conversion with complete selectivity to toluene. At 100°C, 1-SiO$_2$ was able to achieve complete conversion of benzyl alcohol and complete selectivity to the desired HDO toluene product with an average turnover frequency of 7 hr$^{-1}$ over the course of 4 hours.

**Table 4.2:** Catalytic testing of immobilized 1-SiO$_2$ in various solvents for HDO of benzyl alcohol.$^a$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>H$_2$ (bar)</th>
<th>Temp. (°C)</th>
<th>Rxn Press. (bar)$^b$</th>
<th>Convers. (%)$^c$</th>
<th>Select. (%)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>20</td>
<td>25</td>
<td>20</td>
<td>8</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>
Given the catalytic success of with dodecane as the solvent at 100 °C, reproducibility and recyclability of the catalyst was tested at full conversion, and the results of these tests are shown in Table 4.3. The recyclability studies were carried out using the catalytic procedures described in the experimental section. After each reaction the surface modified catalysts were removed from the reaction solution, rinsed, and dried. The reaction mixture was removed from the reactor to allow the reactor to be cleaned, rinsed, and dried as well. A fresh reaction solution was prepared and added to the reactor along with the dried particles from the previous reaction to perform a new reaction. This procedure was repeated with the same catalyst sample for a total of 5 reactions.

Table 4.3: Summary of recycled catalytic and pre-treated results of 1-SiO₂ in dodecane.

<table>
<thead>
<tr>
<th>Rxn Number</th>
<th>Convers. (%)</th>
<th>Toluene (%)</th>
<th>methyl cyclohexane (%)</th>
<th>cyclohexane methanol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>&gt;99</td>
<td>91</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>&gt;99</td>
<td>95</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

---

superscript, e: $8.8 \times 10^{-5}$ mol \( I \) (450 mg total 1-SiO₂) in 25 mL of solvent with 0.1 M benzyl alcohol. Reaction time 4 hrs.

superscript, b: Total pressure inside the reactor during reaction.

superscript, c: Percent conversion of benzyl alcohol.

superscript, d: Percent selectivity for toluene formation.

superscript, e: Other major product detected was benzyl acetate in 16%.
The results for the first recycled catalyst trial (rxn. 2, Table 4.3) show complete conversion of benzyl alcohol was maintained over the 4-hour reaction. It is worth noting that just A300 SiO₂ particles are not catalytic for benzyl alcohol conversion (Table 4.1), thus observing the complete conversion of benzyl alcohol in recycled reactions indicates that the Pd catalysts must still be attached to the surface of the SiO₂ support. Furthermore, 1-SiO₂ exhibits complete selectivity for HDO over ring hydrogenation, whereas, metallic Pd nanoparticles exhibit poor selectivity towards HDO (~ 50 %). For the first recycled catalyst trial (rxn 2, Table 4.3) selectivity towards HDO was less than complete (91 %), but still strongly favored. The other products formed following the second reaction were ring hydrogenated products: methyl cyclohexane in 7 % and cyclohexane methanol in 2 %. Thus, the results of the first recycle trial clearly indicate that the molecular catalyst remained on the surface of the SiO₂ support. However, the reactivity and/or nature of 1-SiO₂ has slightly changed, though complete reduction of all of the molecular catalyst 1 to metal nanoparticles has likely not occurred, as evidenced by the prolonged high selectivity for HDO over ring hydrogenation.

Upon further recycle trials (rxn 3 – 5, Table 4.3), the selectivity did not continue to decrease, but instead stayed at >90 % selectivity for the desired HDO product toluene. Through five recycled reactions, the catalyst also maintained high activity, with complete conversion of benzyl alcohol occurring in four hours for each test. These results are consistent with the molecular catalyst remaining attached to the oxide surface for multiple
catalytic reactions. These results also show that attaching molecular catalysts to the surface of oxide particles greatly increases the ease of catalysis separation and reuse compared to molecular homogeneous catalysis.

To further support that catalytic activity arises from the hybrid molecular/heterogeneous 1-SiO$_2$ catalyst and not from homogenous catalysts that may form in situ from catalyst detachment from the SiO$_2$ support, we tested the reaction solution for catalytic activity. To perform this test, a standard reaction was performed as outlined in the experimental section. After the reaction, the heterogeneous 1-SiO$_2$ catalyst was removed from the reaction mixture. Additional benzyl alcohol was then added to the reaction mixture. The batch reactor was then pressurized with H$_2$ and heated to 100 °C for 4 hours. No consumption of the added benzyl alcohol was observed, and no additional toluene formation was detected. Thus, the heterogeneous catalyst maintains reactivity over several catalytic trails, but the homogeneous solution does not exhibit catalytic activity. Additionally, molecular complex 1 was suspended in dodecane solvent under identical reaction conditions as a test for the detached complex performing catalysis in the absence of SiO$_2$. There was no consumption of benzyl alcohol through the course of a 4-hour reaction. It is therefore concluded that the catalysis observed in this report has arisen from hybrid heterogeneous catalyst 1-SiO$_2$ and there is no evidence for solution homogeneous catalysis during these studies.

The persistent catalyst activity and selectivity over multiple catalyst recycle reactions indicates that small changes in catalyst reactivity occurs after the initial reaction, but the composition and activity of the catalyst remains consistent for multiple subsequent trials. To test this hypothesis, we took a fresh sample of 1-SiO$_2$ and exposed it to 20 bar H$_2$ pressure, at 100 °C for 4 hours without solvent or benzyl alcohol substrate. After this initial
exposure to H$_2$, the 1-SiO$_2$ sample was tested for HDO of benzyl alcohol. The row entitled pre-treated in Table 4.3 shows that the 1-SiO$_2$ exposed to H$_2$ before catalysis performs similarly to the recycled catalyst. Thus, it appears that after the catalyst is exposed to reductive conditions, such as H$_2$ pressure, catalyst activity and selectivity become well defined.

To examine the nature of 1-SiO$_2$ post-reaction, the catalyst was characterized with solid-state NMR, XRD and XPS measurements. Solid-state $^{13}$C NMR of 1-SiO$_2$ after a catalytic reaction still contained peaks with chemical shifts between 160 and 120 ppm indicating the presence of the 2,2':6',2''-terpyridine-4'-carboxylic acid ligand on the surface of the SiO$_2$ support (Figure 4.6). These results show that the ligand is still attached to the surface of SiO$_2$ post reaction. Using dodecane as a solvent likely assists this prolonged attachment as dodecane cannot hydrogen bond to the surface of support nearly as well as the carboxylic acid of the tpy ligand.

![Figure 4.6](image)

**Figure 4.6:** $^{13}$C NMR spectra of 1-SiO$_2$ following a reaction in dodecane showing the presence of the catalyst on the surface of silica
XPS was used to provide useful insight into the functional groups present on the surface of the SiO$_2$.\textsuperscript{60} The binding energy (BE) of carboxylates on the surface of oxides can be found at 288.3 eV\textsuperscript{60} and XPS results of a post reaction sample of 1-SiO$_2$ show a peak at 288.3 eV, clearly indicating the continued presence of the carboxylate linking group in the catalyst samples (Figure 4.7). Additionally, contributions to the C 1s peak due to C--Pd interactions are expected around 282.0 – 283.0 eV.\textsuperscript{61} A C 1s peak was recorded at 283.5 eV suggesting the presence of a weak interaction between carbon and palladium. The XPS spectrum, however, also possibly shows the presence of metallic Pd at 334.4 eV, which is slightly lower than the typical metallic Pd peak at 335.1 eV.\textsuperscript{62} (Figure 4.8)

![XPS spectrum diagram](image)

**Figure 4.7:** Deconvoluted C 1s XPS spectra following a reaction in dodecane showing the...
presence of carboxylate binding energy as well as some C–Pd interaction.

![XPS Pd 3d spectra following a reaction in dodecane showing a very low signal for metallic Pd.](image)

**Figure 4.8:** XPS Pd 3d spectra following a reaction in dodecane showing a very low signal for metallic Pd.

The fact that after pre-treatment of the surface with H₂ and heat, the selectivity of 1-SiO₂ slightly decreased and ring hydrogenated products were observed is consistent with a portion of the molecular catalyst being reduced to metallic Pd. Thus, following a catalytic reaction in dodecane at 100 °C 1-SiO₂ was characterized with XRD. Post reaction analysis showed small peaks corresponding to metallic palladium (Figure 4.9). The presence of nanoparticle, metallic Pd peaks suggests some decomposition of the molecular catalyst 1 to form Pd nanoparticles on the surface of the SiO₂ support. The formation of metallic Pd
nanoparticles is an unwanted side reaction and is likely the result for the small decrease in selectivity observed after recycling the 1-SiO$_2$ catalyst. The selectivity of the recycled catalyst, however, still greatly favored HDO over ring hydrogenation and is much greater selectivity than what is observed with pre-made metallic Pd nanoparticles. The observation of metallic Pd particles in conjunction with observing the 2,2':6',2″-terpyridine-4'-carboxylic acid ligand on the surface of the SiO$_2$ support post reaction with high HDO selectivity over ring hydrogenation leads us to believe only a portion of the molecular catalyst is reduced to Pd nanoparticles under full conversion studies. This partial decomposition of molecular catalysts may be due to a difference in catalyst orientations on the surface as discussed in the computational results.

**Figure 4.9:** Powder X-ray diffraction profiles of fresh A300(red) and 1-SiO$_2$ following a full conversion, 4-hour, 100 °C reaction (green) in dodecane. Metallic Pd peak positions denoted with a diamond with crystal planes denoted above.

To test whether the molecular catalyst decomposed throughout the course of the reaction or only after substrate depletion occurred, catalyst recyclability studies were
performed under limited substrate conversions. The number of low conversion recycle reactions was selected to ensure that 1-SiO$_2$ was tested for the rough equivalent of two full conversion reactions, while simultaneously monitoring the initial selectivity of the catalyst under operating conditions. As can be seen in Table 4.4, under low conversion reactions, the selectivity of 1-SiO$_2$ is maintained for 10 consecutive reactions. Furthermore, the mean turnover frequency for these reactions is 21 hr$^{-1}$. These results indicate that the initial turnover frequency for 1-SiO$_2$ is at least 3 times greater than the average turnover frequency for the full conversion reactions. In addition, no change in catalyst selectivity for HDO of benzyl alcohol was observed over 10 recycled reactions, illustrating the inherent selectivity of the hybrid molecular/heterogeneous 1-SiO$_2$ catalyst.

**Table 4.4:** Low conversion catalyst recycled studies for HDO of benzyl alcohol with 1-SiO$_2$ in dodecane.

<table>
<thead>
<tr>
<th>Rxn Number</th>
<th>Convers. (%)</th>
<th>Select. to Toluene (%)</th>
<th>Select. to methyl cyclohexane (%)</th>
<th>Select. to cyclohexane methanol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.5</td>
<td>&gt;99</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>18.0</td>
<td>&gt;99</td>
<td>0</td>
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<tr>
<td>3</td>
<td>17.7</td>
<td>&gt;99</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>18.4</td>
<td>&gt;99</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>17.6</td>
<td>&gt;99</td>
<td>0</td>
<td>0</td>
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<tr>
<td>6</td>
<td>17.9</td>
<td>&gt;99</td>
<td>trace$^b$</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>21.0</td>
<td>&gt;99</td>
<td>trace</td>
<td>trace</td>
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<td>8</td>
<td>19.4</td>
<td>&gt;99</td>
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<td>9</td>
<td>21.1</td>
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<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>19.8</td>
<td>&gt;99</td>
<td>trace</td>
<td>trace</td>
</tr>
</tbody>
</table>

$^a$4.4x10$^{-5}$ mol 1 (450 mg total 1-SiO$_2$), 30 minutes.

$^b$trace refers to signals that equate to less than 1% of the carbon balance.
We examined the 1-SiO$_2$ catalyst used for the low-conversion studies with XRD to look for the presence of Pd nanoparticles. The XRD pattern (Figure 4.10) does not show evidence for Pd nanoparticles on the SiO$_2$ supports. While the lack of observed XRD patterns for Pd nanoparticles does not definitely conclude the lack of Pd nanoparticles, the lack of the observed peaks in the XRD pattern is different from the data obtained after the full substrate conversion reactions, where clear evidence for Pd nanoparticles existed. Overall, these studies are consistent with the hypothesis that the molecular catalyst 1 maintains attachment to the SiO$_2$ support and remains active for selective HDO as long as the substrate remains in excess. Upon substrate depletion, the molecular catalyst can be reduced by H$_2$ down to metallic Pd nanoparticles. These nanoparticles are an unwanted side reaction that produces a material which lacks the desired catalytic selectivity.

**Figure 4.10:** Powder X-ray diffraction profile of 1-SiO$_2$ following the low conversion, 30-minute, 100 °C catalytic reactions (red) in dodecane. No signals for metallic Pd peaks are present.
With an understanding of the catalyst stability and activity determined with benzyl alcohol substrate, the HDO of additional oxygenated aromatic substrates was explored and the results are shown in Table 4.5. Catalyst $1$-$\text{SiO}_2$ exhibited high activity and selectivity for the hydrodeoxygenation of vanillyl alcohol and vanillin at the benzylic position without any observed ring hydrogenation. Deoxygenation of the phenolic or methoxy group directly on the aromatic ring of these substrates was not observed. This reactivity is consistent with the lack of reactivity we observed between $1$-$\text{SiO}_2$ and $p$-cresol. The catalytic HDO of benzaldehyde to form toluene was also performed with full selectivity for HDO. Lastly, a complete lack of ring hydrogenated products was also observed for the catalytic conversion of benzophenone to diphenylmethane. However, after 4 hours under catalytic conditions, the major product observed was diphenylmethanol, the product of ketone hydrogenation. Extending the reaction time to 24 hours increased the yield of diphenylmethane and the overall conversion of benzophenone. These results show that the $1$-$\text{SiO}_2$ catalyst hydrodeoxygenates ketones via a two-step process where the ketone is hydrogenated to the alcohol, followed by hydrodeoxygenation of the alcohol.

**Table 4.5:** Catalytic activity of $1$-$\text{SiO}_2$ in dodecane for HDO of various oxygenated aromatic compounds.$^a$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$H_2$ (bar)</th>
<th>Temp. (°C)</th>
<th>Rxn Press. (bar)$^b$</th>
<th>Convers. (%)$^c$</th>
<th>Select. (%)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>20</td>
<td>100</td>
<td>23</td>
<td>88</td>
<td>$&gt;99^e$</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>20</td>
<td>100</td>
<td>23</td>
<td>90</td>
<td>15$^f$</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>20</td>
<td>100</td>
<td>23</td>
<td>$&gt;99^g$</td>
<td>67$^f$</td>
</tr>
<tr>
<td>Vanillyl Alcohol</td>
<td>20</td>
<td>100</td>
<td>23</td>
<td>$&gt;99$</td>
<td>$&gt;99^h$</td>
</tr>
<tr>
<td>Vanillin</td>
<td>20</td>
<td>100</td>
<td>23</td>
<td>&gt;99</td>
<td>&gt;99h</td>
</tr>
<tr>
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<td>------</td>
</tr>
</tbody>
</table>

\(^a\)8.8 \times 10^{-5} \text{ mol I} (450 \text{ mg total 1-SiO}_2) \text{ in 25 mL of solvent. Reaction time 4 hrs.}\n
\(^b\)Total pressure inside the reactor during reaction.

\(^c\)Percent conversion of substrate.

\(^d\)Percent selectivity HDO product formation.

\(^e\)Desired product is toluene.

\(^f\)Desired product is diphenylmethane, other major product observed is diphenylmethanol.

\(^g\)Reaction time = 24 hr.

\(^h\)Product observed is creosol.

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**Catalyst and Amorphous Silica Interaction Characterization**

Computations were performed to gain further insight into the interaction(binding) between molecular catalyst 1 and the surface of the amorphous silica support. Attachment of molecular catalysts to oxide supports has been previously reported,\(^40\), \(^43\) but little quantitative information is still known about the interaction between the molecular units and the oxide surface. Since the mode and the strength of binding of complexes onto the support surface cannot be easily probed experimentally, we utilize first-principles simulations. In particular, we used a model of amorphous silica and evaluated the interaction energy (IE) between that model and the catalyst complex. To gain further insight through a comparative study, complex 2 (Figure 2) was also computationally probed. Figure 4.11 shows contour plots of the IE in vacuo for both complexes 1 and 2. The stronger binding ability of the former complex compared to the latter correlates with the acidity strength of the carboxylic group (pK\(_a\) = 1.31 for complex 1, and 3.87 for complex 2). This correlation indicates the more acidic linker group can form stronger H–bonds with the surface of the silica. The qualitative trends of the IE are largely the same for both catalysts, indicating that the characteristic of the binding is determined by the local amorphous silica structure. Therefore, we will only discuss complex 1. From the scan of the amorphous surface, five sites with large IE (-25 to -50 kcal mol\(^{-1}\)) were located, shown
in Figure 3a with the letter A-E. Since these five sites demonstrated strong binding, we used them as model sites to investigate the mode of binding more in detail.

![Contour plots](image)

**Figure 4.11:** Contour plots of the interaction energy (kcal mol$^{-1}$) for a) complex 1 and b) complex 2. Sites labeled A-E have the largest interaction energies.

The analysis of the hydrogen bonding patterns on sites A-E from the semi-rigid scan allows us to gain some initial information about the type and strength of the hydrogen bonding. We found three schemes that represent strong H bonding (HB): 1. COH—O(silanol), 2. COH—O(siloxane), and 3. C=O—H(silanol). The hydrogen bonding length, the O–O length, and the corresponding interaction energy for complex 1 in the unrelaxed configurations are shown in Table 4.6.

**Table 4.6:** H bond distance (Å) of Sites A-E between the carboxylate linker and the silica surface for three schemes of H-bonds of complex 1: 1) COH—O of a SiOH group; 2) COH—O of a SiOSi group; 3) C=O—H of a SiOH group. O—O are the distances of the oxygens participating in the H bond.

<table>
<thead>
<tr>
<th>Site</th>
<th>IE$^a$</th>
<th>Scheme 1</th>
<th>Scheme 2</th>
<th>Scheme 3</th>
<th>O—O</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-26.9</td>
<td>1.04</td>
<td>-</td>
<td>1.97</td>
<td>2.45*</td>
</tr>
<tr>
<td>B</td>
<td>-47.0</td>
<td>1.62</td>
<td>-</td>
<td>-</td>
<td>2.63</td>
</tr>
<tr>
<td>C</td>
<td>-29.4</td>
<td>-</td>
<td>2.37</td>
<td>-</td>
<td>3.32</td>
</tr>
<tr>
<td>D</td>
<td>-28.4</td>
<td>-</td>
<td>2.10</td>
<td>-</td>
<td>3.10</td>
</tr>
</tbody>
</table>
Site A presents two hydrogen bonds, following Schemes 1 and 3, but the IE value is smaller than all the others because the O-O distance is too short, which leads to unfavorable Coulombic interaction between the partial negative charge on the O centers. This strained configuration is due to the fixed orientation of the complex and the surface, where only the carboxylic and silanol groups are allowed to adjust. Site B follows HB Scheme 1, and it has a strong interaction energy due to a short HB length. Sites C, D and E follow HB Scheme 2. Site E has a larger IE than C and D by 4 kcal mol\(^{-1}\), likely due to its 0.6 Å shorter HB, as indicated in Table 4.6.

Given that the initial scan has revealed a number of strong binding sites, we can now focus on these sites to investigate the relative orientation of the complex on the silicate surface. In particular, we focused on Sites A, B, D, and E for the geometrical relaxation of the complex on the surface. Site C is not further considered, as the hydrogen bonding distances and IE value are very similar to site D. The internal coordinates of the catalyst were kept frozen, but the catalyst itself is allowed to move as a rigid body. Sites A and B hydrogen bond through Scheme 1 and relax to a geometry in which the SiOH is protonated by COOH to make water. A proton from another SiOH protonates the C=O and forms SiOSi. The carboxylate group remains in the same position as in the rigid scan, hydrogen bonding with the water and SiOSi, but the catalyst itself becomes parallel to the surface. Sites D and E hydrogen bond through Scheme 2 and also become parallel to the surface, as shown in Figure 4.12. Overall, the computations predict that an isolated complex tends to lay parallel to the surface regardless of the hydrogen bonding schemes, consistent with previous work.\(^{63-64}\) While these initial results do not corroborate the experimental data,
other possibilities must be considered. For a single complex H-bonded to the surface, the IE for the relaxed orientations are much larger than those found from the rigid geometry scan in solvent, as shown in Table 4.7. In fact, the relaxed IE values become comparable to the semi-rigid values in vacuo. The IE values may be due to a combination of dispersion effects of the π-conjugated ligand with the surface, and Coulombic attraction between the positively charged metal and the surface. We discriminated between these two possible effects by repeating the geometry optimization without the Pd center. Without Pd, the IE decreases by 4-9 kcal mol\(^{-1}\), but the complex still optimizes to lay parallel to the surface. It is worth noting that the calculations focus on a single molecule, but high surface coverage may limit the space available for each complex to interact with the surface in a parallel orientation, thus favoring an upright orientation.

<table>
<thead>
<tr>
<th>Site</th>
<th>IE Rigid(^{a})</th>
<th>IE Relaxed(^{a})</th>
<th>IE Relaxed (No Pd)(^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.7</td>
<td>-28.8</td>
<td>-25.8</td>
</tr>
<tr>
<td>B</td>
<td>-14.2</td>
<td>-78.4</td>
<td>-69.2</td>
</tr>
<tr>
<td>D</td>
<td>-12.6</td>
<td>-35.1</td>
<td>-29.1</td>
</tr>
<tr>
<td>E</td>
<td>-13.9</td>
<td>-37.8</td>
<td>-33.0</td>
</tr>
</tbody>
</table>

\(^{a}\)kcal mol\(^{-1}\)

Geometry optimizations were run on another possibility that the complex covalently bonds to the surface through the linker group via a dehydration reaction,\(^{65}\) which may also prevent the laying-down orientation due to steric effects. As a result of covalently linking 1 to the amorphous silica surface both in the perpendicular and parallel configurations, the catalyst preferred to stand up upon optimization as can be seen in Figure 4.13. The computation results of covalently binding the complex to the silica surface agree
more closely with the metal loading via ICP-MS as well as the catalytic HDO results, which suggest there are molecular complexes persistently present.

**Figure 4.12:** Example of a relaxed orientation of 1-SiO$_2$ in the parallel configuration

**Figure 4.13:** Example of a relaxed orientation of 1-SiO$_2$ in the perpendicular conformation
Conclusions

The hybrid molecular/heterogeneous catalysts \(1-\text{SiO}_2\) and \(2-\text{SiO}_2\) were prepared and compared for initial activity towards the selective hydrodeoxygenation of benzyl alcohol. Upon determination that \(1-\text{SiO}_2\) was the better performing catalyst, it was characterized and utilized in a further catalytic study for hydrodeoxygenation of other oxygenated aromatics. Spectroscopic evidence for the molecular catalyst attached to the surface of \(\text{SiO}_2\) was supported by computational studies that indicate two or more orientations of the molecular catalyst on the silica surface are likely present. In either presented orientation, the calculated binding energies are in agreement with the experimental finding that these molecular catalysts can be attached onto the surface of amorphous silica for prolonged reactivity. While the experimental results suggest that the catalyst prefers to stand in a perpendicular orientation to the surface of silica, computations on an isolated complex suggests that a single complex prefers to lay parallel to the surface. Further calculations are necessary with a larger quantity of complexes to mimic experimental results, however this approach is computationally expensive.

The molecular catalyst attached to the silica support exhibited excellent selectivity towards HDO and did not result in any observed ring hydrogenation. This catalytic selectivity can be attributed to ensuring a lack of the extended catalyst surfaces typically encountered with metallic nanoparticle catalysts. Recyclability studies showed consistent product formation could be obtained over multiple catalytic runs. Under substrate depletion, however, partial decomposition of the catalyst led to the unwanted formation of metallic nanoparticles and a decrease in overall product selectivity. Maintaining excess substrate was able to overcome catalyst decomposition routes and lead to prolonged catalyst lifetime and selectivity. The reactivity of the catalysts for HDO of benzylic
positions was excellent, but catalyst activity towards HDO of phenolic oxygen atoms needs to be improved. With the ability to fine tune molecular catalysts through well-known synthetic modifications, this hybrid catalyst motif offers a new avenue for selective, catalytic HDO of oxygenated aromatic compounds important for lignin upgrading.

**Experimental**

**Materials**

N,N-Dimethylformamide (DMF) (anhydrous, 99.9 %, VWR), methanol (MeOH) (99.8 %, VWR), dodecane (anhydrous, 99 %, Sigma-Aldrich), acetic acid (glacial, Fisher Scientific) were purchased and used without any further purification as solvents for catalyst synthesis, immobilization and catalytic testing. Dichloro(1,5-cyclooctadiene)palladium(II) (Oakwood Chemical) was used as the palladium precursor for catalyst synthesis. 2,2’:6’,2”-terpyridine-4’-carboxylic acid (tpy-COOH) (95 %, Alfa Aesar) and 4-([2,2’:6’,2”-terpyridin]-4’-yl) benzoic acid (tpy-C₆H₄COOH) (98%, TCI) was purchased and used as the ligand to synthesize complexes suitable for immobilization. Aerosil 300 (A300, Evonik) was used as the metal oxide support for the molecular catalyst. A300 is amorphous SiO₂ with 300 m²/g surface area and an average particle size of 20 nm. Tetraamminepalladium(II) chloride (99.99 %, Aldrich) was used as the palladium precursor for nanoparticle preparation. SBA-15 (ACS Material) was used as the silica support for the nanoparticles. SBA-15 is a mesoporous silica with <150 μm particle size and a surface area of 540 m²/g. Benzyl alcohol (99 %, Alfa Aesar), benzaldehyde (98 %, Alfa Aesar), benzophenone (99 %, Acros), vanillyl alcohol (98 %, TCI) and vanillin (99 %, Alfa Aesar) were purchased as used as a model substrate for catalytic testing without any purification. Hydrogen (H₂) (>99.95 %, Praxair) was used as the hydrogen source during catalytic testing.
Catalyst Preparation

\[ \text{PdCl}((2,2',6',2''-\text{terpyridine})-4'-\text{carboxylic acid})\text{Cl} \quad (1) \]

Dichloro(1,5-cyclooctadiene)palladium (0.285 g, 1 mmol) and tpy-COOH (0.277 g, 1 mmol) were added to a 9:1 mixture of MeOH and DMF (100 mL) and stirred at reflux for 1 hour and allowed to cool to room temperature. The yellow-orange precipitate that formed was filtered and washed with cold MeOH and allowed to dry. Yield: 0.40 g (0.88 mmol, 88%). \(^1\)H NMR (DMSO-d$_6$, ppm): 9.005 (s, 2H), 8.900 (d, 2H), 8.760 (dd, 2H), 8.471 (dt, 2H), 7.935–7.899 (m, 2H). \(^1^3\)C NMR (DMSO-d$_6$, ppm): 164.68, 158.03, 155.91, 152.55, 144.87, 143.15, 129.70, 126.54, 124.27. Elemental analysis for PdC$_{16}$H$_{11}$N$_3$O$_2$Cl$_2$ (1) calculated: C 42.27 %, H 2.44 %, N 9.24 %. Found: C 41.47 %, H 2.53 %, N 8.91 %.

\[ \text{PdCl}(4-((2,2',6',2''-\text{terpyridin})-4'-yl)\text{benzoic acid})\text{Cl} \quad (2) \]

Dichloro(1,5-cyclooctadiene)palladium (0.285 g, 1 mmol) and tpy-C$_6$H$_4$COOH (0.353 g, 1 mmol) were added to a 9:1 mixture of MeOH and DMF (100 mL) and stirred at reflux for 1 hour and allowed to cool to room temperature. The red precipitate that formed was filtered and washed with cold MeOH and allowed to dry. Yield: 0.54 g (0.846 mmol, 84%).

Complex 1 or 2 (50 mg) was dissolved in 100 mL DMF and sonicated to ensure complete solubility. Immediately following, A300 (1.0 g) was added to the DMF solution and sonicated for 10 minutes to ensure a well-dispersed suspension. The resulting mixture was allowed to sit undisturbed for 12+ hours to allow the complex to interact with the surface of the silica particles. Following the soak period, the solution/suspension mixture is filtered and washed with cold MeOH to remove any excess DMF and allowed to air dry. Following this procedure, the resulting solids were characterized to ensure the molecular nature of the
catalyst remained intact and attached to the surface of the A300 support. 1-SiO$_2$ supported on A300 has a yellow tint to it while 2-SiO$_2$ bears a reddish tint (Figure 3.11), both indicative of the color of the molecular complexes. $^{13}$C SSNMR of 1-SiO$_2$ (500 MHz, ppm): 164.35, 155.81, 152.04, 142.22, 140.16, 129.93, 126.65, 124.07.

**Palladium nanoparticles supported on mesoporous silica (Pd/SBA-15)** was prepared by the method of strong electrostatic adsorption with synthesis conditions based on previous work. The Pd on the support powder was calculated to be 1.3 wt% Pd/SBA-15. The XRD patterns for the support and final catalyst give a particle size estimation of very small particles equal to or less than 1 nm.

**Instrumentation**

X-ray diffraction (XRD) analysis was carried out with a benchtop powder X-ray diffractometer (Rigaku Miniflex-II with a silicon strip detector, D/teX Ultra – capable of detecting nanoparticles down to 1.5 nm) with Cu Kα radiation ($\lambda = 1.5406$ Å), operated at 15 kV and 30 mA. Powder samples were loaded on a zero-background holder and scans were made from the 20 – 80 °2θ range, with a scan rate of 3.0 °2θ/min. Solution-phase NMR analysis was taken on a Bruker Avance III-HD (400 MHz). Solid-state NMR analysis was taken on a Bruker Avance III-HD (500 MHz). Inductively Coupled Plasma-mass spectrometry (ICP-MS, Finnigan ELEMENT XR double focusing magnetic field) analysis was used for the analysis of palladium present on silica with rhenium as internal standard. Quartz torch and injector (Thermo Fisher Scientific) and 0.2 mL/min Micromist U-series nebulizer (GE, Australia) were used for sample introduction. X-ray photoelectron spectroscopy (XPS) measurements were performed using an XPS system (Kratos AXIS Ultra DLD with a monochromatic Al Kα source), operated at 15 keV and 150 W and a hemispherical energy analyzer. The X-rays were incident at an angle of 45° with respect to
the surface normal. Analysis was performed at a pressure below $2 \times 10^{-9}$ mbar. High resolution core level spectra were measured with a pass energy of 40 eV. The XPS experiments were performed while using an electron gun directed on the sample, for charge neutralization. Post-reaction products were analyzed through GC-MS (Shimadzu QP-2010S). The separation column was a 30-meter-long Rxi-5ms (Restek) with a 0.25 mm id and the oven temperature program was 40°C for 0.5 minutes followed by a 10°C/min ramp to 280°C and held for 2 minutes. Mass spectrometer electron ionization was at 70 eV and the spectrometer was scanned from 500 to 50 m/z at low resolution.

* Catalytic Testing – General Procedure

All reactions were carried out in a 130-mL capacity stainless steel batch reactor (Parker Autoclave Engineers). For a typical experiment, 260 µL (0.10 M) benzyl alcohol, and 450 mg (2.1 wt. % Pd, $8.8 \times 10^{-5}$ mol) catalyst were mixed in 25 mL of the chosen solvent. The resulting mixture was then sealed in the batch reactor and purged with 25 bar H$_2$ three times. Then, the reactor was filled to the desired pressure of H$_2$ and kept sealed for the duration of all experiments. For reactions that required elevated temperatures, a heating jacket was used for heating, with a thermocouple for temperature control. The reaction was then stirred at 900 rpm for the duration of the experiment. Following the experiment, the reactor was allowed to cool to room temperature without stirring and the pressure released. Products of reactions were analyzed through GC-MS following filtration of the catalyst.

* Catalytic Testing – Recyclability Testing/Low Conversion

All recyclability testing was carried out in a 130-mL capacity batch reactor following the general procedure above. Following each reaction, the solid, heterogeneous catalyst was filtered from the reaction solution, rinsed multiple times with hexanes, and
dried. A new reaction solution was then prepared, according to the general procedure above. The dried, recycled catalyst was then added to the new reaction solution and the catalytic reaction was carried out under identical conditions to the first catalytic reaction. The procedure was chosen to ensure that product formation from multiple catalytic cycles could only arise from the heterogeneous catalyst system, and that catalysis was not occurring in homogeneous solution.

Low conversion studies were carried out in similar fashion as described in the general procedure; however, the amount of catalyst was decreased to 225 mg (2.1 wt. % Pd, 4.4x10^{-5} mol) and the reaction time was decreased to 30 minutes. Low conversion recyclability was achieved through the same means as described above for the full conversion recycle tests.

**Computational Protocol**

As the binding of the catalyst on an amorphous surface depends on the local structure of the surface, it is difficult to determine a single structure of the silicate that is representative of the experimental conditions. Therefore, we started by systematically scanning various possible binding sites of catalyst 1 on a large slab of amorphous silicate. The latter is obtained with a procedure based on molecular dynamics simulations, described in previous work.\(^6\) The scan is performed maintaining both the complex and the silicate surface at a fixed distance and almost completely rigid, in order to determine the most favorable sites for, and modes of binding quickly. Once the strongest binding sites are located with this fast procedure, we focused only on these and we let the complex relax on the surface. The internal complex structure is kept rigid to limit the computational effort. In this way, we determined the energetics and geometry of catalyst immobilization.
Figure 4.14: Complex 1 as it is oriented in regard to a silica surface prior to running geometry optimizations. The dashed blue line indicates the average height of the highest 10 atoms. Teal spheres are Pd, blue is N, light gray is C, dark gray is Si, red is O and white is H.

The complex, seen in Figure 4.14, was placed perpendicular to the surface of the silicate cluster, at a fixed distance of about 3 Å. Since the cluster surface is irregular, the 10 highest atoms were selected, and the average position of the z-coordinate perpendicular to the surface of the top 10 atoms was chosen for analysis. We then placed the C atom of the carboxylate group 3 Å above this average z-coordinate. This procedure places the catalyst close enough to the surface to allow hydrogen bonding with nearby silanol groups. We then performed a constrained geometry optimization where only the carboxylate group and the pre-existing silanol groups are allowed to relax. The interaction energy (IE) is calculated as:

$$IE = E_{\text{Complex} \text{--} \text{Site}} - (E_{\text{Complex}} + E_{\text{Site}})$$
The system is treated using the B3LYP hybrid functional and Grimme’s D3 dispersion correction.\textsuperscript{67} The Pd is treated with the Def2TZVP basis set and Stuttgart’s pseudopotentials.\textsuperscript{68} The groups that are most likely to contribute to the IE, the carboxylate group and pre-existing silanols at each site, are treated with 6-31++g(2d,p). This basis set includes diffuse functions to better describe the hydrogen bonding interactions between the silica and the linker group. The remaining atoms were treated with the 6-31g(d) basis set. The IE were calculated both in vacuo and in the presence of DMF, using geometries that are relaxed in the corresponding medium. The solvent effect is described with the solvation model with density approach (SMD).\textsuperscript{69}

The four sites with the largest IE are used for an additional geometry optimization in which the catalyst orientation on the silicate surface is allowed to relax. The relaxation is performed in DMF while keeping the internal structure of the complex rigid.

In order to interpret the properties that lead to catalyst binding to the surface we also computationally examined a derivative of catalyst 1. The derivative, catalyst 2, was chosen to investigate how relatively minor changes in the complex structure may affect the binding ability. As discussed earlier, the binding is related to the pK\textsubscript{a} of the benzoic acid moiety. The pK\textsubscript{a} values were calculated using the method by Thapa and Schlegel, which includes two explicit water molecules and implicit aqueous solvation.\textsuperscript{70-71} The pK\textsubscript{a} calculations were also performed with B3LYP, the Def2TZVP basis set and Stuttgart’s pseudopotentials for Pd, and the 6-31+g(d,p) basis set for all other elements. All calculations were performed with a development version of the GAUSSIAN suite of programs.\textsuperscript{72}
References


CHAPTER 5

CONCLUSIONS AND FUTURE OUTLOOK
Conclusions

The work presented in this dissertation encompassed a number of advancements in the field of catalytically upgrading lignin-derived monomeric units. Preliminary insight was gained in the advancement of feasible routes towards useful chemicals and fuels from biomass-derived sources, specifically lignin.

The use of silanes to protect alcohol functional groups to allow for the production of higher value chemicals from alcohol-containing molecules. Through the use of a mild-base catalyzed process, the hydrosilylation of various alcohols was reported ranging from aliphatic alcohols to substituted aromatic alcohols that more closely resemble the monomeric units that are present in lignin. This silylation process is an improvement of silylation chemistry that has been reported previously, however it's use in lignin chemistry is limited and in need of exploration. It is important to develop routes towards higher value chemicals from oxygenated aromatics as mentioned previously, due to the lack of thought placed into their use in today’s technology. The development of a milder process for the silylation of alcohols opens avenues to different areas of chemistry for lignin-derived aromatic alcohols. The silylation of alcohols can provide a protecting group for the functionalization of the aromatic ring without sacrificing the alcohol present on the ring when it comes to producing polymers or other synthetic products from biomass.

Upgrading lignin-derived monomers can also be through the production of fuels. This process can be carried out through catalytic hydrodeoxygenation as was reported in Chapters 3 and 4. An example of selective hydrodeoxygenation through the use of a homogeneous catalyst: chloro(2,2′:6′,2″-terpyridine)palladium(II) chloride was shown to be highly active for benzylic oxygenated aromatic molecules. A mechanism has been proposed to rationalize the process by which this catalytic reaction takes place, through the
formation of a palladium–hydride species. The determination of whether or not this mechanism is the pathway by which catalysis occurs will be discussed in the next section. This palladium catalyst exhibited conversions of benzyl alcohol to toluene under conditions as mild as room temperature and 10 bar H₂. While activity was low under these very mild conditions, a small increase in the hydrogen pressure (20 bar) and temperature (100 °C) afforded complete conversion of benzyl alcohol to toluene in just 4 hours. The calculated turnover frequency of 5.0 hr⁻¹ for benzyl alcohol and benzaldehyde were comparable to previously reported reactions, however with much higher selectivity towards the desired aromatic product. While the homogeneous catalysis was successful in performing hydrodeoxygenation of benzylic substrates, catalyst separation and recyclability was a challenge that was addressed.

The molecular catalysts chloro(2,2‘:6’,2”-terpyridine-4’-carboxylic acid)palladium(II) chloride and chloro([-([2,2′:6′,2″-terpyridin]-4’-yl) benzoic acid)palladium(II) chloride were prepared and supported on high surface area SiO₂ to provide for an easier post reaction separation of catalyst from reaction mixture. Not only did the development of this catalyst motif provide for an easier catalyst separation, the catalyst was now recyclable over multiple reactions without any observed loss in activity. Despite this, some catalyst decomposition occurs leading to ring-hydrogenated side products, further work can be carried out to provide added stability to these catalysts in the future. The supported catalyst 1-SiO₂ was shown to be a more effective catalyst for the selective hydrodeoxygenation of benzylic oxygenates than its counterpart 2-SiO₂. The observed catalytic activity of the support molecular catalyst was inferior to the homogeneous catalyst under identical reaction conditions. Fortunately, the supported molecular catalysts afforded the opportunity to explore a variety of solvents to carry out
the reaction, as solubility was no longer a critical factor for the catalyst. It was found that a nonpolar solvent, dodecane provided the highest catalytic activity, averaging 7.0 hr\(^{-1}\) through the course of a 4-hour reaction. An improvement on the average turnover frequency for this catalyst was observed through low conversion studies of hydrodeoxygenation of benzyl alcohol. The initial turnover frequency observed through a 30-minute reaction while using just half the catalyst was 21 hr\(^{-1}\), preliminarily showing that the catalyst’s initial turnover frequency is much higher than what is observed over the full 4-hour period. This further work is required to determine an optimal reaction time that would elucidate the kinetics of catalytic hydrodeoxygenation over supported molecular catalysts.

**Future Outlook**

The work presented in this dissertation encompassed a number of advancements in the field of catalytically upgrading lignin-derived monomeric units from the use of a mild base for the silylation of alcohols, to the use of palladium organometallic catalysts for the selective hydrodeoxygenation of model lignin monomers.

In Chapter 2, the mild base, \(\text{K}_2\text{CO}_3\) was used to catalyze the silylation of various aromatic and aliphatic alcohols using a number of different hydrosilanes. While this work largely examined the silylation process itself, the investigation of these of silylated products as building blocks in polymer synthesis is feasible. Additionally, the use of silylated alcohols as larger leaving groups than \(\text{H}_2\text{O}\) in hydrodeoxygenation reaction is another route that warrants experimental investigation. Silylated alcohols could provide means to perform hydrogenolysis of the silyl ether, generating a hydrocarbon product and a silanol side-product as shown in Figure 5.1. Utilizing silylated alcohols has the potential
to be impactful in the field of lignin upgrading both as building block material and as a facilitator for the selective hydrodeoxygenation processes discussed in this dissertation.

![Proposed reaction of the hydrogenolysis of a silyl ether](image)

**Figure 5.1:** Proposed reaction of the hydrogenolysis of a silyl ether

This work also showed early examples of selective hydrodeoxygenation of benzylic oxygenates through the use of a homogenous catalyst. Additionally, the development of supported molecular catalysts for the same transformation opens the door to new possibilities in the realm of catalytic hydrodeoxygenation. While these are promising results there remains a significant amount of understanding to be gained, especially as it pertains to the mechanism and catalytic activity of the catalysts presented in this work.

In chapter 3, the homogeneous catalyst chloro(2,2′:6′,2″-terpyridine)palladium(II) chloride was used to selectively deoxygenate benzylic oxygenates. A proposed catalytic mechanism was presented, however further studies into the intermediates formed and the catalytic pathway are still required to support this proposed mechanism. The proposed mechanism can be investigated by attempting to isolate a Pd–hydride complex with the use of $\text{H}_2$ or another hydride source, followed by a subsequent reaction with benzyl alcohol. While this is the proposed mechanism, it must also be kept in mind that this catalysis takes place in a reducing environment, which presents an alternative pathway through the reduction of the Pd complex to then interact with the oxygenated molecule, which may ultimately prove to be the pathway by which this catalysis takes place.

The study on chloro(2,2′:6′,2″-terpyridine-4′-carboxylic acid)palladium(II) chloride supported on a heterogeneous silica support is far from completed. While the use of supported molecular catalysts have been studied for various other processes, the viability
for thermally activated processes is still lacking. First, the determination of the kinetics of the catalyst will be studied to achieve a deeper understanding of catalyst activity as it compares to heterogeneous catalysis examples of hydrodeoxygenation. Initial calculations have shown that the kinetics of the supported molecular catalyst are faster than the homogenous catalyst counterpart.

Furthermore, the means by which the catalyst is prepared can be altered to achieve higher activity and/or stability. First, the metal present within the terpyridine ligand can be changed to present a more stable complex under the reducing conditions that catalysis takes place. Metals that can be used rather than palladium include ruthenium and cobalt. While both analogs of the catalyst have been prepared, neither has been extensively studied as of yet. Secondly, the attachment of the ligand to metal oxides supports can be manipulated to strengthen the binding of the catalyst to the surface. As was mentioned in Chapter 4, other functionalities that can be used to attached molecular complexes to oxide surfaces are phosphonates and hydroxamates. Despite carboxylates have been used in this work, their binding is thought to be weaker than the counterparts listed above. It seems to be a logical approach to attempt to synthesize molecular complexes with a variety of binding groups to determine the differences in stability under a variety of reaction conditions.

Modifications to the catalyst structure itself have been discussed, however manipulating the surface at which the catalyst binds is another route that could be explored. In this work, silica was used as the solid support for the catalyst. However other solid metal oxide supports could be used to attach the catalyst that display differing characteristics that may play a role in observed reactivity, such as zirconia, titania and tin oxide could be explored for their ability to stabilize the catalytic system.
Aside from directly modifying the constituents of the catalyst itself, other approaches could be taken to provide added stability to the catalyst in the effort to perform more difficult transformations. One method that could be employed is atomic layer deposition (ALD), which would provide solid metal oxide layers that could immobilize the catalyst in place on the surface, thus adding stability to the catalyst-surface interaction.

All of the proposed modifications to the catalyst presented in Chapter 4 have kept the goal of deoxygenating aromatic molecules that are derived from, or closely related to lignin monomers. While this catalyst exhibited reactivity towards sp³–C–O deoxygenation, sp²–C–O remains an elusive target. Further extensions of this work presented in this dissertation should help develop the field of lignin upgrading, specifically the deoxygenation pathways discussed.
References

APPENDIX A

NMR SPECTRA OF NEWLY SYNTHESIZED SILYLATED ALCOHOLS
Figure A.1: $^1$H NMR spectrum of compound 2a in CDCl$_3$
Figure A.2: $^{13}$C NMR spectrum of compound 2a in CDCl₃
Figure A.3: $^{29}$Si NMR spectrum of compound 2a in CDCl$_3$
Figure A.4: $^1$H NMR spectrum of compound 4b in CDCl$_3$
Figure A.5: $^{13}$C NMR spectrum of compound 4b in CDCl$_3$
Figure A.6: $^{29}\text{Si}$ NMR spectrum of compound 4b in CDCl$_3$
Figure A.7: $^1$H NMR spectrum of compound 18 in CDCl$_3$
Figure A.8: $^{13}$C NMR spectrum of compound 18 in CDCl$_3$
Figure A.9: $^{29}$Si NMR spectrum of compound 18 in CDCl$_3$
Figure A.10: $^1$H NMR spectrum of compound 19 in CDCl$_3$
Figure A.11: $^{13}$C NMR spectrum of compound 19 in CDCl$_3$
Figure A.12: $^{29}\text{Si}$ NMR spectrum of compound 19 in CDCl$_3$
APPENDIX B

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