



Low temperature selective hydrodeoxygenation of model lignin monomers from a homogeneous palladium catalyst

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ABSTRACT

The molecular, homogeneous catalysts $[\text{Pd}(\text{tpy})\text{Cl}]\text{Cl}$ and $[\text{Ni}(\text{tpy})](\text{PF}_6)_2$, 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 $[\text{Pd}(\text{tpy})\text{Cl}]\text{Cl}$ 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.

1. 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 Fig. 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 [11,12]. This provides motivation for research into the upgrading of lignin-derived monomers through the selective removal of oxygenated substituents.

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 [13]. However, the chemical structure of lignin displays potential to be used as a viable chemical feedstock through depolymerization to monomeric units [5]. 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 [2,14]. 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 [15–20]. 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 [21]. 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

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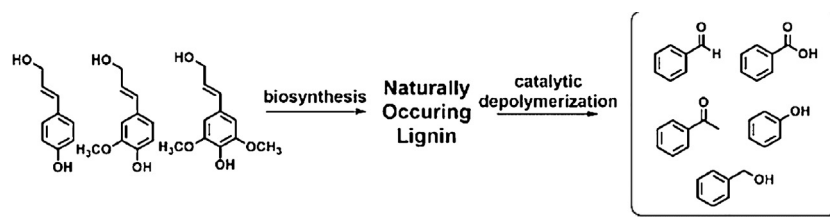


Fig. 1. General scheme for the synthesis of lignin followed by depolymerization and some commonly formed monomeric units.

targeted oxygenated substituents. Selective deoxygenation of benzaldehyde and benzyl alcohol has been achieved via electrochemical [22,23] and photochemical methods [24]. 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 [25,26]. Additionally, the activation of C–O bonds in aryl compounds has also been investigated through the use of homogeneous systems [27,28]. 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 [26,28]. 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].

The chemical structure of the homogeneous catalysts utilized in this work can be found in Fig. 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 ($T = 25\text{ }^{\circ}\text{C}$ – $200\text{ }^{\circ}\text{C}$, $P = 10$ – 20 bar H_2). 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 H_2 molecule, followed by selective hydrodeoxygenation of the model substrates.

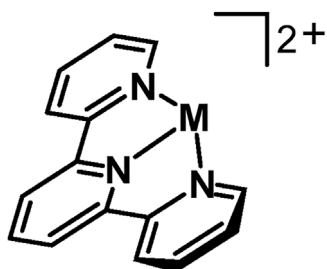


Fig. 2. Structure of metal-terpyridine catalysts. M = Ni, Pd.

2. Materials and methods

2.1. Materials

Methanol (MeOH) (99.8%, VWR) was used as the solvent for all catalysis reactions. K_2PdCl_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.

2.2. GC–MS

Gas chromatography was performed on a HP-5890 GC (Agilent). The separation column was a 30-m-long Rtx-5 (Restek) with a 0.25 mm id and the oven temperature program was $50\text{ }^{\circ}\text{C}$ for 3 min followed by a $10\text{ }^{\circ}\text{C}/\text{min}$ ramp to $300\text{ }^{\circ}\text{C}$. 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.

2.3. NMR

^1H NMR spectroscopy was performed using Bruker Avance III HD 300. NMR data were processed by Bruker's TopSpin software. Reference DMSO peak for ^1H NMR was defined as 2.50 ppm.

2.4. Synthesis

$[(2,2':6',2''\text{-terpyridine})\text{PdCl}]\text{Cl}$ was synthesized via an adapted procedure from Yilmaz [30]. K_2PdCl_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 h. 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%). ^1H 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).

$[(2,2':6',2''\text{-terpyridine})\text{Ni}](\text{PF}_6)_2$ was synthesized according to literature procedure [31].

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 [32]. SBA-15 support ($\text{SA} = 1270\text{ m}^2/\text{g}$) was added to an aqueous solution of Tetraammine-palladium(II) chloride, $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$. 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 $120\text{ }^{\circ}\text{C}$ 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.

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