



Research paper

Electrochemical conversion of lignin to useful chemicals



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ABSTRACT

Electrochemical conversion of waste lignin from pulping mills and biorefineries is an alternative renewable process for generating industrial chemicals that may afford better control over conversion than other catalytic or thermochemical processes because the electrode potential, and hence the reaction energetics, can be controlled. The authors report here electrochemical oxidation of lignin on a Co core/Pt partial shell nanoparticle alloy electrocatalyst, identify several oxidation products, and quantify oxidation product concentration as a function of oxidation time. Key results show that useful chemicals like heptane and apocynin are generated during the electrochemical oxidation of lignin. Some key oxidation product concentrations increase steadily over time, suggesting they are likely stable products that do not participate in other reactions. Concentrations of other oxidation products increase and then decrease with time, suggesting that they may participate in proceeding chemical or electrochemical reactions. Formation of other oxidation products like 1,3-bis(1,1-dimethylethyl)-benzene and 1,4-di-tert-butyl-phenol suggest oxidative decomposition initiated by hydroxyl radicals that are likely generated at the anode. Overall, the results suggest that electrochemical oxidation of lignin is complex, with possibly many competing homogeneous chemical and heterogeneous electrochemical reactions.

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1. Introduction

Lignin, a highly branched natural organic polymer which gives structural support to plants, is an underutilized biomaterial that currently enjoys few applications other than as a low-grade fuel for generating heat in pulping processes. After cellulose, lignin is the most abundant renewable carbon source; it has been estimated that between 40 and 60 million tons are produced annually, mostly as a non-commercialized waste product [1]. Interestingly, lignin's complex structure, composed of many linked aromatic groups, means that it holds potential as a renewable feedstock for a variety of industrial chemicals and liquid fuels. From highly functionalized monomeric or oligomeric aromatic products, which can be used as starting materials for pharmaceutical and chemical processes [2], to liquid fuels, lignin's oxidation valorization is potentially wide-ranging. Its abundance as the primary waste from biorefineries and the kraft pulping process [3–6] means that it could potentially replace a significant amount of fossil raw materials, such as petroleum, as a renewable feedstock for a host of chemicals, with substituted aromatics among the most interesting. Several

methods have been examined to convert lignin to more useful chemicals, including gasification in supercritical water [7,8], catalytic steam reforming at high temperatures [9], oxidative pyrolysis [10], catalytic hydrodeoxygenation and hydrocracking [11], hydrothermal fragmentation and condensation [12], and gasification in aqueous solutions over Pt catalysts [13]. In general, though, such processes have not been able to overcome limitations such as achieving selective oxidation [4] and generation of solid residue like char [14]. Such catalytic processes are often difficult to control, and commercial viability has not been demonstrated.

In contrast, electrochemical pathways provide a measure of control over oxidation of complex organic compounds [15], with the potential to narrow oxidation products down to a particular molecular weight range by controlling 1) the oxidation potential (hence, reaction energetics) and/or 2) oxidation time. In addition, electrochemical conversion of lignin is potentially more environmentally friendly than some other processes because conversion takes place in moderately alkaline solutions at low to moderate temperature and pressure and electrons driving the reaction can be described as non-polluting reagents [15]. For these reasons, electrochemical conversion of lignin is an interesting process and one that deserves attention.

There have been some significant efforts related to electrochemical oxidation of lignin [16–34]. Specifically, Wang and co-

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workers presented results on the electrocatalytic degradation of aspen lignin on Pb/PbO₂ electrodes [35]. They identified 4-methylanisole as the main product of lignin oxidation, and hypothesized that hydroxide radicals ($\cdot\text{OH}$) oxidize lignin, a conclusion they reached by considering the earlier work of Quiroz and co-workers on oxidation of *p*-nitrophenol on similar electrodes [36], i.e., its well-known activity toward generating $\cdot\text{OH}$ radicals that can in turn oxidize other species. Hao and co-workers have recently investigated similar routes toward lignin degradation on PbO₂ electrodes modified with [Fe(CN)₆]³⁻ [37]. They quantified lignin degradation by UV–vis, and found that removal efficiencies approached 50% after 2 h.

These results followed the comprehensive review by Lange and co-workers on lignin conversion routes, which also discussed the likely electrochemical route mediated by $\cdot\text{OH}$ radicals. Considering recent mechanistic knowledge, one should target electrocatalysts that readily lead to $\cdot\text{OH}$ radical formation. Pt [38] and Co [39] have both been noted for electrochemical generation of $\cdot\text{OH}$ radicals.

This group has recently published results indicating that electrochemical oxidation of lignin on NiCo alloy electrocatalysts follows quasi-reversible behavior, with modification likely from oxidation of hydroxyl groups present in lignin's guaiacyl units a main contributor to lignin oxidation [40]. That study presented spectroscopic evidence of lignin degradation, but it did not identify oxidation products as it was not within the scope of the work at that time.

The present study reports the electrochemical oxidation of lignin at Co core/Pt partial shell alloy electrocatalysts. This paper focuses on determining some mechanistic parameters of lignin oxidation, such as reversibility, and attempts to identify oxidation products and their concentration as a function of time under constant-potential oxidation conditions.

2. Experimental

2.1. Materials

Lignin (10,000 g/mol) was purchased from Sigma–Aldrich and used as received. CoCl₂·H₂O, H₂PtCl₆ solution (8 wt% in H₂O), and ethylene glycol (EG) were purchased from Sigma–Aldrich. NaOH and KOH were acquired from Fisher Scientific and Vulcan XC-72 carbon was obtained from Cabot. All materials were used as received.

2.2. Electrocatalyst synthesis

Co core/Pt partial shell alloy nanoparticles were synthesized using the so-called polyol method. First, 0.44 g of CoCl₂ and 0.7 g of Vulcan XC-72 carbon were dissolved in 50 and 25 mL of EG, respectively. Then, these solutions were added under stirring to a round flask containing 25 mL of EG and heated to 80 °C for 1 h. Subsequently, 7 g of NaOH previously dissolved in 30 mL of EG were added to the mixture, which was heated under reflux at 80 °C for an additional hour. After that, the temperature was increased to the boiling point (~185 °C) for 2 h and then cooled to room temperature. The Co/C nanoparticles were recovered via filtration, washed several times with DI water, and dried in an oven at 60 °C overnight. For Pt partial shell deposition, 0.5 g of Co/C catalyst (dissolved in 25 mL of EG), 0.7 mL of H₂PtCl₆ solution and 0.2 g NaOH (dissolved in 25 mL EG) were added under stirring to a round flask containing 25 mL of EG. The mixture was heated at 80 °C for 2 h, and then the temperature was increased to 160 °C for 6 h. After reduction, the Co core/Pt partial shell alloy electrocatalyst was washed and dried following the procedure described above for the Co/C base. Finally, the granular material was crushed to a fine powder using a mortar.

2.3. Electrocatalyst characterization

X-Ray diffraction (XRD) patterns on the Co/C and Co core/Pt partial shell alloy electrocatalysts were obtained on a Rigaku Ultima IV Diffractometer using a Cu K α -source (40 KV/44 mA). The data were collected with a scan rate of 1°/min. The particle size was calculated by the Scherrer equation, using the standard Rigaku PDXL software.

2.4. Electrochemical measurements

The electrocatalyst was suspended in an equal volume solution of ethanol and water so that the concentration was 1 mg of catalyst per mL of 1:1 ethanol:water mixture. After ultrasonication to disperse the electrocatalyst in the 1:1 ethanol:water mixture, 25 μg of electrocatalyst was suspended drop-wise on a Pt rotating disk electrode (RDE); the ethanol:water solution was evaporated by gently heating the Pt RDE in a typical laboratory oven at 70 °C until only the electrocatalyst remained on the disk. Electrochemical measurements were conducted in a standard three-electrode beaker cell, with the Co core/Pt partial shell alloy electrocatalyst as the working electrode. A Hg/HgO electrode served as the reference, and a Pt ring positioned 2 cm away from the working electrode served as the counter electrode. Although the reference electrode was Hg/HgO, the potentials were later referenced against the standard hydrogen electrode (SHE) for analysis and reported as such in this work. The electrochemical experiments were conducted at room temperature and under atmospheric conditions. Cyclic voltammetry was conducted in 1 M KOH at 0.05 V/s in the absence of lignin as a background. Next, lignin was added to the alkaline solution so that its concentration was 10 g of lignin per liter, and cyclic voltammetry was conducted at scan rates ranging from 0.05 V/s to 0.5 V/s. Then, the RDE with the Co core/Pt partial shell electrocatalyst was rotated from 200 rpm to 1700 rpm and the potential of the working electrode was scanned for kinetic studies. Finally, the working electrode potential was held constant at 0.598 V vs. SHE, and solution was periodically pipetted and stored in a vial to identify oxidation products via GC–MS.

2.5. Identification of lignin oxidation products

A ThermoFisher Trace 1300 ISQ GC–MS with a 60 m TraceGOLD GC column (0.25 mm ID, 0.25 μm film) was used to identify the lignin oxidation products from the standard NIST database included with ThermoFisher's Chromeleon software. Oxidation samples collected during constant-potential oxidation, as described above, were neutralized with H₂SO₄ and the oxidation products were extracted into chloroform. Oxidation samples were injected into the GC–MS with the following protocol: 1:75 split, hold at 50 °C for 3 min, ramp at 10 °C per minute to 270 °C, hold for 20 min. The peak areas of the oxidation products as calculated by the Chromeleon software were compared to the peak area of a reference standard (2-fluorophenol) at 500 ppm to estimate product concentrations, assuming that nearly all of the volatile oxidation products were extracted into chloroform upon neutralization of the oxidation product solution. The product concentrations were measured as a function of time to determine changes in the product stream during constant-potential oxidation, and product generation rates were determined as a function of electrocatalyst loading (mass of electrocatalyst in the system).

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