Catalytic Depolymerization of Lignin via Supported Nanoparticles

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Global energy demands have rapidly increased over the past two centuries, corresponding to great consumption of fossil fuels such as coal, natural gas, and oil.[1] Burning these fossil fuels results in carbon dioxide emissions, which has a negative impact as a greenhouse gas.[1] For several reasons including the carbon dioxide emissions, there has been a large effort to replace fossil fuels with renewable energy. One benefit of fossil fuels are the byproducts: cheap feedstock chemicals including benzene, toluene, and xylenes.[1] Decreasing the fossil fuel usage would cause an increase in the prices of feedstock chemicals, causing price inflations for goods such as pharmaceuticals, paint, and plastics unless another inexpensive source of these chemicals can be found.[2]

Lignin is a renewable resource that shows promise as a source of aromatic feedstock chemicals; however, degradation into aromatic chemicals is challenging.[2] Lignin is a phenolic and polydisperse biopolymer located in plant cell walls charged with protecting the hemicellulose and cellulose from degradation. During paper pulping processes, carbohydrates are removed, leaving behind lignin as the waste byproduct.[3] Most degradation methods shown in Figure 1 incorporate air-sensitive catalysts, caustic chemicals, high temperatures, or high pressures.[4] Hydrogenolysis consists of the cleavage of a C-C or C-heteroatom bond using H_2 and a catalyst. This is an efficient and selective process of cleaving ether bonds in lignin without caustic chemicals, high temperatures, or radical mechanisms.[4] There are three main classes of catalysts for the hydrogenolysis of lignin: homogeneous catalysts, heterogeneous catalysts, and bioenzymatic catalysts. Homogenous catalysts have been shown to be very effective using model complexes, but efficiency greatly decreases with lignin samples.[4] Bioenzymatic catalysts like β-etherases strongly rival supported nanoparticles with catalytic activity, but there are many challenges towards industrializing the process such as overall costs.[5] Out of the viable heterogeneous catalysts, supported nanoparticles have gained attention due to high yields of monophenol products, air and water-stability, and low byproduct yields.[3]

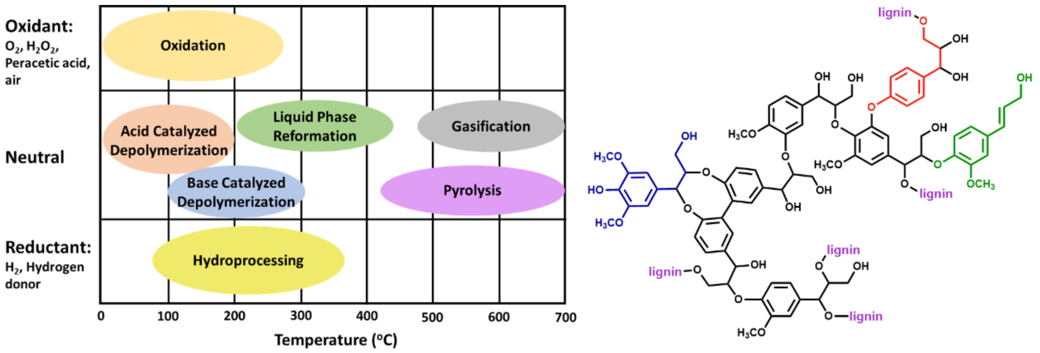

Figure 1: A summary of lignin depolymerization reactions (left) and the structure of lignin (right).[4]

Commonly used commercial precious metal catalysts include Ru, Pd, Pt, and Rh nanoparticles on carbon support.[3] Van der Bosch et al. hydrogenolyzed birch wood using Ru/C to produce 52% monophenols.[6] The Pd/C catalyst has been used for lignin from birch, poplar, and high-syringyl transgenic poplar, generating 48%, 59%, and 70% yield of monophenols respectively.[7,8] Precious metal catalysts have shown excellent catalytic activity; however, more abundant metals like Ni, Cu, or Mo are being pursued to lower overall costs.[9] Ni is an attractive alternative as it activates H_2 more readily than Cu and Mo.[10] Song et al. reported using Ni/C and birch wood to produce 54% monophenols; however, these results were not replicated by Klein et al. who reported a 32% yield with a higher catalyst loading.[11,12]

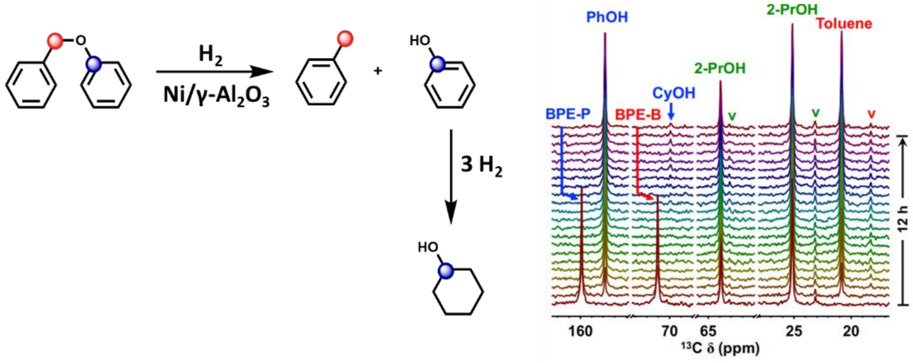

Figure 2: Scheme of ^{13}C labeled biphenyl ether degradation with ^{13}C NMR hydrogenolysis data.[10]

Alternate support systems than carbon have been reported such as zeolites, alumina, and silica (SBA-15, a specific hexagonal structure of silica).[4] Ni/SBA-15 and Pd/SBA-15 were used to hydrogenolyze corn stover lignin yielding 4.2 and 5.7 wt% monophenols respectively.[3] Qui et al. investigated the degradation mechanism of Ni/γ-Al_2O_3 using the model complex biphenyl ether (BPE) by selectively labeling the phenolic and benzylic carbons (Figure 2).[10] Hydrogenolysis of BPE was followed by subsequent hydrogenation of phenol to cyclohexanol.[10] The Ni/γ-Al_2O_3 catalyst system was not attempted with lignin samples, but the determined 40 minute latency period was attributed to reducing a thin NiO layer to Ni^0 for the reaction to progress.[10]

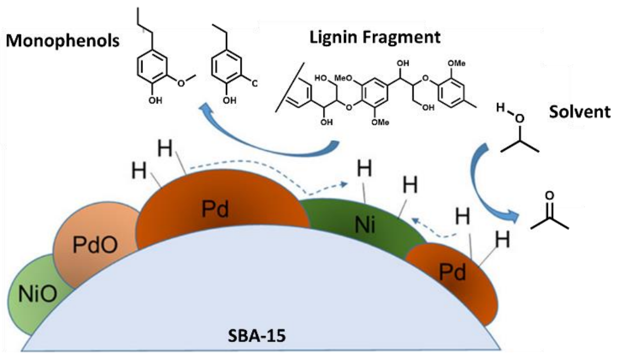

Figure 3: Synergistic $Pd_{50}Ni_{50}$/SBA-15 capable of hydrogen abstraction from isopropanol.[3]

Monometallic non-precious metal systems have not been able to achieve higher product yields than the commercial systems so recent focus has shifted towards bimetallic systems. Zhu et al. demonstrated calcination of an M-gallate metal-organic framework (MOF) to produce $Ni_{0.5}Co_{0.5}$/C with lower energy costs.[9] The $Ni_{0.5}Co_{0.5}$/C catalyst with poplar lignin yielded 55.2% monophenols, higher than that demonstrated with Ni/C, leading the authors to propose a synergistic effect.[9] One disadvantage of hydrogenolysis is the excess of H_2 required, but there have been recent successes with abstracting H_2 from solvent.[3,4] Jiang et al. investigated the

$Pd_{50}Ni_{50}$/SBA-15 system shown in Figure 3.[3] Using corn stover lignin, $Pd_{50}Ni_{50}$/SBA-15 produced 8.1 wt% monophenols, which was 2 times greater than Ni/SBA-15 and 1.4 times that of Pd/SBA-15.[3] Hydrogen abstraction was proposed to occur on Pd active sites followed by hydrogen continually spilling over onto Ni active sites (Figure 3).[3] Adsorption of hydrogen is followed by lignin chemisorption and ether bond cleavage.[3]

In conclusion, precious metal catalysts have shown excellent catalytic activity, but Ni supported nanoparticle systems have begun approaching similar yields for the depolymerization of lignin into aromatic feedstocks. Specifically, bimetallic Ni systems show a synergistic effect between the metals, allowing for high yields with low hydrogenation byproducts, and activity with alternate hydrogen donors. Going forward, more knowledge about lignin degradation mechanisms is necessary as well as overall recyclability of the catalyst and additional co-catalyst systems.

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