Catalytic Lignin Valorization to Monomeric Phenols & High Value Chemicals

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Abstract

Lignin is a three-dimensional, amorphous, polyphenolic and aromatic-rich material, and is a primary recalcitrant molecule in lignocellulosic biomass. Unlocking valuable chemicals and fuel molecules from lignin requires the cleavage of typical inter-unit linkages like β–O–4, α–O–4 and 4–O–5 in a selective manner. This presentation will focus on catalytic hydrogenolysis process to selectively convert lignin to high value C6-C9 monomeric phenols like guaiacols, alkyl guaiacols and guaiacyl alcohols. Over the years, we have developed a range of novel Pd-metal oxides (Al, Zr, Mo, and W)-supported activated bio-char (ABC) catalysts for depolymerization of lignin to propyl guaiacol. High selectivity to alkyl guaiacols was observed with Pd-Al/ABC, while the presence of W and Mo inhibited the hydrogenation of the aliphatic C_α=C_β bond. At the optimum condition, high selectivity to 4-propyl guaiacol (38%) was observed with Pd-Al/ABC. The addition of transition metals to Pd altered the chemoselective hydrogenation (C_α=C_β) and dehydroxylation (C_γ–OH) of C9 monomeric guaiacols. Based on quantum chemical calculations, the hydrogenation of C_α=C_β is shown to be catalyzed by the Pd^0 active site, while the dehydroxylation of C_γ–OH is catalyzed by the transition metal. The use of these catalysts for catalytic transfer hydrogenolysis of lignin using hydrogen donor co-solvents will also be discussed. Our recent works are focused on deriving C9 phenols directly from biomass using reductive catalytic fractionation (RCF) process, which is a one-pot "lignin-first" approach. We have demonstrated selective recovery of propyl guaiacol with high retention of the carbohydrates from pine wood biomass using a range of (Ni, Ru, Pd, Pt)/activated carbon catalysts. Interesting results in this direction will also be discussed.

Keywords: Lignin, reductive catalytic fractionation, hydrogenolysis, activated carbon, mechanism.

Useful References: Gurrala et al., *Fuel* **308** (2022) 121818. Gurrala et al., *Bioresource Technology* **344** (2022) 126204. Kumar et al., *Molecular Catalysis* **530** (2022) 112532. Prabhudesai et al., *Sustainable Energy and Fuels* **7** (2023) 2117.