# LIGNIN DEPOLYMERIZATION USING NITRATE-INTERCALATED LAYERED DOUBLE HYDROXIDE CATALYSTS

Jacob S. Kruger[1], Nicholas S. Cleveland[1], Shuting Zhang[1], Rui Katahira[1], Brenna A. Black[1], Gina M. Chupka[1], Mary J. Biddy[1], Gregg T. Beckham[1*]

[1]National Renewable Energy Laboratory
Golden, CO 80401

*Abstract*

We have evaluated a series of layered double hydroxide (LDH) catalysts based on Mg-Al hydrotalcites for aromatic monomer production from lignin model dimers and process-relevant herbaceous lignin streams. LDH catalysts that have been partially exchanged with nitrate anions show high activity and are easily regenerable. The reaction solvent plays a strong role in the product spectrum, and GPC results show that the best catalysts generate a significant fraction of low-molecular weight products.

*Keywords*

Lignin depolymerization, layered double hydroxide, nitrate ion exchange.

## Introduction

Lignin is an abundant renewable polymer that consists of phenylpropanoid units connected by a variety of linkages, including several types of aryl ethers and aryl alkyl bonds. Lignin has long been considered a promising source of renewable aromatic chemicals, but its valorization has been hindered by a lack of catalytic strategies to effectively depolymerize the material to monoaromatic components.

Layered Double Hydroxides (LDHs) are materials based on platelets of edge-sharing $M(OH)_6$ octahedra with a nominal stoichiometry of $M(OH)_2$, where M is typically an alkaline earth or first-row transition metal. These platelets are stacked, and the space between platelets, called the interlayer space, contains water of hydration. While the material is stoichiometric with divalent metals, trivalent or higher metals can be substituted to some degree, which introduces a charge imbalance in the $M(OH)_2$ layers. This imbalance is remedied by the presence of anions in the interlayer space. One well-known example of this class of materials is hydrotalcite (HTC), with the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot xH_2O$. The HTC structure is visualized in Figure 1.
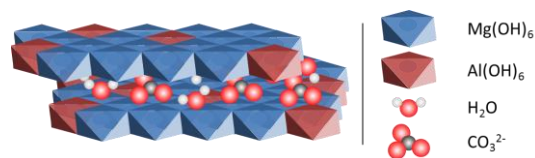


*Figure 1. Schematic representation of the hydrotalcite structure.*

LDHs can exchange metals and anions, leading to a catalytic activity in a wide range of reactions. We recently showed that hydrotalcite loaded with $Ni(NO_3)_2$ as an ethanolic solution was active for aryl ether cleavage in a lignin model compound and could reduce the molecular weight of two herbaceous lignin streams. (Sturgeon, 2014) This initial work motivated us to explore the source of the catalytic activity and the versatility of these catalysts in more detail.

---

[*] To whom all correspondence should be addressed

## Results

To determine the source of catalytic activity, we initially screened different metals and anions in the reaction of a lignin model dimer, 2-phenoxy-1-phenylethanol (PE), to phenol and acetophenone. The reaction is shown in Figure 2.



2-Phenoxy-1-phenethanol (PE)    Acetophenone    Phenol

*Figure 2. Reaction of β-O-4 model dimer PE over hydrotalcite catalysts.*

As shown in Figure 3, all of the catalysts prepared from nitrate precursors showed high activity for this reaction, while all those prepared from chloride precursors did not. Additionally, a catalyst prepared by ion exchange of $NO_3^-$ anions into the interlayer space is also active, even with no transition metal present. Thus, the $NO_3^-$ anion is the primary source of catalytic activity.
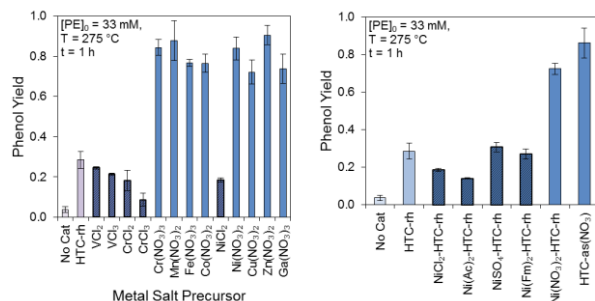


*Figure 3. Phenol yield from PE over HTC catalysts prepared from different metal precursors and with different counteranions.*

The catalyst maintains activity through at least two reaction cycles, after which the activity decreases. However, the activity can be restored by replenishing the nitrate reservoir in the interlayer space.
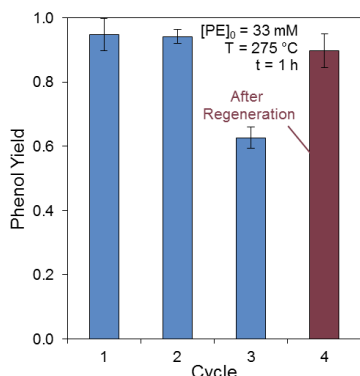


*Figure 4. Phenol yield through multiple catalytic cycles, showing regeneration by replenishing the nitrate reservoir.*

When these catalysts are applied to isolated lignin streams, such as a deacetylated, disc-refined, enzymatically hydrolyzed (DDE) lignin from corn stover, the molecular weight distribution clearly shifts to lower molecular weights, as shown in Figure 5. The catalytic activity is apparent when the solvent is water or 3-methyl-3-pentanol (3M3P). The main products in water are phenol, guaiacol, and syringol, along with smaller amounts of vanillin, syringaldehyde, acetovanillone, and acetosyringone. In 3M3P, the main product is 4-vinylphenol, as shown in Figure 6.
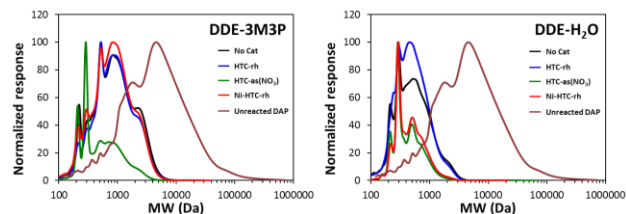


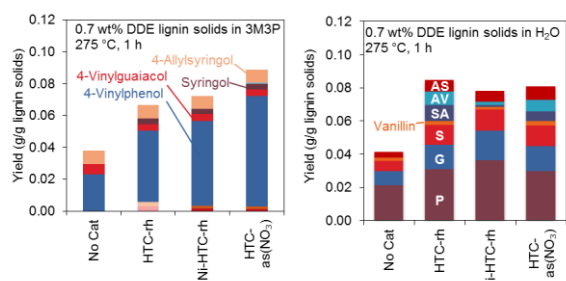*Figure 5. GPC results from corn stover lignin reacted over nitrate-intercalated HTC catalysts.*



*Figure 6. Monomer yields of compounds detected by GC-MS from DDE corn stover lignin. P = phenol; G = guaiacol; S = syringol; SA = syringaldehyde; AV = acetovanillone; AS = acetosyringone.*

## Conclusions

Hydrotalcite catalysts intercalated with nitrate anions are active for β-O-4 bond cleavage in lignin model compounds and are active for depolymerization of isolated corn stover lignin. These materials represent a promising new catalytic strategy for the production of renewable fuels and chemicals from lignin.

## Acknowledgments

## References

Sturgeon, M. R., O'Brien, M.H., Ciesielski, P.N., Katahira, R., Kruger, J.S., Chmely, S.C., Hamlin, J., Lawrence, K., Hunsinger, G.B., Foust, T.D., Baldwin, R.M., Biddy, M.J., Beckham, G.T. (2014). Lignin Depolymerisation by Nickel Supported Layered Double Hydroxide Catalysts. *Green Chem.*, 16, 824.