

# Base promoted hydrogenolysis of lignin model compounds and organosolv lignin over metal catalysts in water

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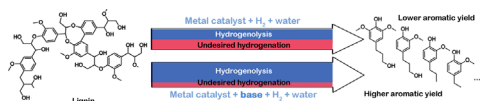
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## HIGHLIGHTS

- The first systematic study of base promotional effect in lignin hydrogenolysis.
- Lignin hydrogenolysis into aromatics was carried out in pure water under mild conditions.
- The yield for monomeric aromatic compounds from lignin increased ca. 100% in the presence of base.
- Base promotional effect was observed over Ru (a typical noble metal) and Ni (a typical non-noble metal) catalysts.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Herein we present a systematic investigation on the promotional effect of base in metal catalysed hydrogenolysis of lignin model compounds and organosolv lignin. The research started with the evaluation of pH effects (pH 1–14) on the hydrogenolysis of a lignin  $\beta$ -O-4 model compound over a Ru catalyst (a stable catalyst over a wide pH range), from which a significantly increased selectivity towards monomeric compounds was observed in the presence of base. This promotional effect was studied in detail over bimetallic  $\text{Ni}_7\text{Au}_3$  nanoparticles. Addition of a strong base such as NaOH significantly enhanced the activity and selectivity for C–O bond hydrogenolysis over undesired hydrogenation reactions, not only in lignin model compounds but also in real lignin conversion. Notably, the yield for monomeric aromatic compounds from lignin over  $\text{Ni}_7\text{Au}_3$  catalyst increased ca. 100% after adding NaOH as a promoter, under the same reaction conditions. Mechanistic study suggest that addition of base significantly reduced the benzene ring hydrogenation activity of the metal catalysts. The effect of adding different bases over various metal catalysts were also investigated.

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## 1. Introduction

Recently, the valorisation of biomass, such as lignin, (Perlack, 2005; Huber et al., 2006; Corma et al., 2007; Stöcker, 2008; Yan

et al., 2010; Long et al., 2012; Long et al., 2013; Mu et al., 2013; Sammons et al., 2013) cellulose (Ngee et al., 2014; Siankevich et al., 2014; Yabushita et al., 2014) and chitin, (Dutta et al., 2004; Chen et al., 2014; Pierson et al., 2014) as sustainable alternative for energy, fuel and chemical production becomes cumulatively interesting. Lignin is the most abundant natural aromatic polymer. New methods that can process lignin into value-added aromatic chemicals are highly desirable. (Sales et al., 2007; Marshall and Alaimo, 2010; Zakzeski et al., 2010; Murat Sen et al., 2012; Azadi

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et al., 2013; Ben et al., 2013; Gao et al., 2014) Lignin consists of interlinked arylpropane units with various functional groups like ethers, methoxy and hydroxyl groups, as well as C–C linkages. The most abundant lignin linkage is the  $\beta$ -O-4 linkage with 45–50% occurrence in softwood and even more than 60% in hardwood. Other important ether linkages include the  $\alpha$ -O-4 and 4-O-5 linkages with 4–9% and 6–7% abundance in hardwood, respectively.(Chakar and Ragauskas, 2004; Zakzeski et al., 2010).

The complex structure of lignin necessitates the employment of model compounds bearing typical linkages in lignin to study the reactivity behaviour (see Fig. 1 for typical C–O linkages in lignin). Although no model compounds can precisely represent the lignin structure, this strategy facilitates the understanding of reaction pathways and mechanisms. The difficulty in breaking the ether bonds in lignin model compounds largely depend on the C–O bond energies.  $\alpha$ -O-4 type of linkages are the weakest with a aliphatic C–O bond dissociation energy between 156 to 203 kJ/mol, followed by the  $\beta$ -O-4 linkage (226–303 kJ/mol) and the 4-O-5 lignin linkage (346 kJ/mol).(Dorrestijn et al., 2000; Parthasarathi et al., 2011; Younker et al., 2011) The linkages containing C–C bonds possess even higher bond dissociation energies.(Dorrestijn et al., 2000; Parthasarathi et al., 2011; Younker et al., 2011).

Hydrogenolysis of C–O linkages(Kobayashi et al., 2011; Nakagawa and Tomishige, 2012) in lignin, where  $H_2$  is used to cleave the C–O bond in the presence of a metal catalyst, is regarded as an effective way to transform lignin into depolymerized aromatic platform compounds.(Ruppert et al., 2012; Li et al., 2013; Yan and Dyson, 2013) The complexity of lignin structures makes its depolymerisation a challenging issue and needs the use of appropriate catalysts.(Zakzeski et al., 2010) Early reports date back in 1938 as Harris and Adkins used copper-chromium catalyst for the hydrogenolysis of pretreated aspen hardwood.(Harris et al., 1938) Afterwards Raney Ni,(Baker and Hibbert, 1948; Brewer et al., 1948) Pd, Rh and Ru supported on carbon or  $Al_2O_3$ , and Cu-doped porous metal oxide(Barta et al., 2010; Matson et al., 2011; Barta et al., 2014) have been tested.(Pepper and Lee, 1969; Pepper and

Fleming, 1978; Pepper and Supathna, 1978) High-temperature approaches were generally applied in these earlier reports to break down the polymer structure catalytically. A clear trend in recent study is the development of catalysts that could be operated under milder conditions in environmentally benign solvents, among which heterogeneous nickel catalysts are of particular interest.(Song et al., 2012; Song et al., 2013; Song et al., 2013) In our group a series of bimetallic NiM ( $M=Au, Ru, Rh, Pd$ ) catalysts were developed that exhibited better performance in lignin hydrogenolysis than single component Ni catalyst, among which NiAu catalyst appears to be most effective.(Zhang et al., 2014).

Undesired benzene ring hydrogenation is a severe problem in lignin hydrogenolysis,(Song et al., 2013) which induces increased hydrogen consumption and decreased efficiency. Moreover, benzene ring hydrogenation leads to stable fully saturated products which do not readily undergo further hydrogenolysis.(He et al., 2012; Zhang et al., 2014) In a few literatures it appears the involvement of a base could improve the selectivity towards monomeric aromatics. For example,  $NaO^tBu$  is found to be crucial for a Ni carbene complex catalyzed hydrogenolysis of lignin model compounds.(Sergeev and Hartwig, 2011; Sergeev et al., 2012) Wang and Rinaldi reported that a solvent which exhibits high Lewis basicity results in the formation of aromatics over saturated products over Raney Ni in the conversion of lignin model compounds and organosolv lignin.(Wang and Rinaldi, 2012) Other reports followed, concerning hydrogenolysis reactions over heterogeneous catalysts in the presence of base.(Ren et al., 2013; Zaheer et al., 2014) Despite these encouraging results, some questions remain: (I) what is the pH-activity correlation of the reaction, under otherwise identical conditions? (II) what is the optimized pH for the reaction? (III) what is the role of the base? Does the base enhance the rate of C–O bond hydrogenolysis, or does it inhibit benzene ring hydrogenation, or both? Therefore we carried out detailed studies on the influence of pH in lignin hydrogenolysis over Ru and NiAu catalysts. As mentioned above,

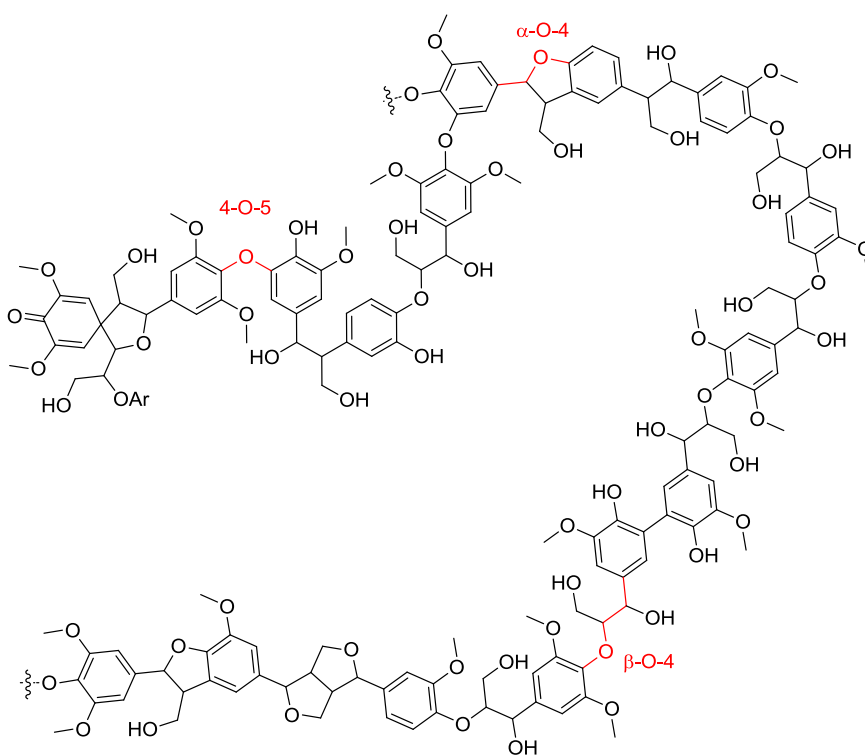


Fig. 1. Schematic fragment structure of hardwood lignin. (Zakzeski et al., 2010).

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