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Catalytic transfer hydrogenolysis of organosolv lignin using B-containing FeNi alloyed catalysts

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ABSTRACT

In this work, FeB, NiB, and FeNiB nanomaterials were examined as catalysts for catalytic transfer hydrogenolysis (CTH) using supercritical ethanol (sc-EtOH) as the hydrogen donor and reaction solvent. The earth-abundant alloys were synthesized using simple aqueous chemical reductions and characterized using ICP-OES, XRD, and STEM-EDS. Using acetophenone to model the desired catalytic reactivity, FeNiB was identified as having superior reactivity (74% conversion) and selectivity for complete deoxygenation to ethylbenzene (84%) when compared to the monometallic materials. Given its high reactivity and selectivity for deoxygenation over ring saturation, FeNiB was screened as a lignin valorization catalyst. FeNiB mediates deoxygenation of aliphatic hydroxyl and carbonyls in organosolv lignin via CTH in sc-EtOH. A combination of gel permeation chromatography, GC/MS, and NMR spectroscopy was used to demonstrate the production of a slate of monomeric phenols with intact deoxygenated aliphatic side chains. In total, these results highlight the utility of CTH for the valorization of biorefinery-relevant lignin using an inexpensive, earth-abundant catalyst material and a green solvent system that can be directly derived from the polysaccharide fraction of lignocellulosic biomass.

1. Introduction

Lignin is a multiaromatic heteropolymer produced by plants to provide strength and rigidity and to aid in water conduction. Since it is a renewable source of aromatic hydrocarbons, lignin is a potential platform for these valuable chemical synthons that are used in the production of myriad fine chemicals and products. Accordingly, several investigations have focused on the catalytic valorization of lignin in the context of the integrated biorefinery [1–5]. Recently, researchers have focused on so-called reductive catalytic fractionation (RCF), which is a family of processes that use various catalysts to upgrade lignin directly from whole biomass in a reducing environment [6–12]. Another related strategy for biomass valorization is based on organosolv fractionation, which first separates whole biomass into its major constituent fractions of cellulose, hemicellulose, and lignin [13,14]. This methodology allows direct upgrading of components, which is an operationally attractive scheme for lignin valorization, given that the tunable process parameters allow for the isolation of lignin with specific properties [15].

Hydrogenolysis reactions of alcohols and carbonyls to produce alkanes are important in the context of biomass conversion to fuels and platform chemicals [16,17]. Since the oxygen content of biomass is substantially higher than that of those products, scalable and economical hydrodeoxygenation (HDO) reactions are needed to produce infrastructure-compatible products. Fractionation of biomass combined with HDO of the resulting fractions allows for condensed-phase deoxygenation strategies to produce fuels, chemicals, and materials at scale. However, because the solubility of H_2 in many organic solvents is low [18], high temperatures and excessive pressures of hydrogen gas are often required for liquid-phase HDO reactions of biomass fractions.

Owing to the safety concerns and operational complexity of high-pressure condensed-phase hydrogenations at scale, a vast body of research has been dedicated to transfer hydrogenation reactions [19]. In these schemes, a molecule (or equivalent) of H_2 is transferred from a donor molecule to the reducible acceptor molecule. Hydrogen donor molecules are oftentimes inexpensive organic alcohols that can be

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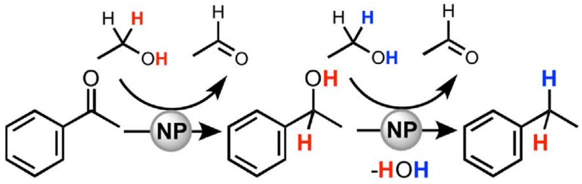

Scheme 1. CTH of acetophenone in ethanol using a hypothetical nanoparticle (NP) catalyst.

directly derived from biomass. These liquid hydrogen donor molecules can also serve as the reaction solvent for hydroprocessing schemes. Under the right conditions (e.g. above the solvent critical point), HDO via transfer hydrogenation can occur (Scheme 1). Supercritical fluids simultaneously display the solvating power of a liquid and the penetrating power of a gas, and have been investigated as reaction media for myriad catalytic reactions involving conversion of biomass and its fractions [20,21]. For example, Ford and co-workers have shown the utility of supercritical methanol for the catalytic transfer hydrogenolysis (CTH) of furans and lignin using Cu-based metal oxide catalysts [22,23].

Although several examples of materials capable of mediating CTH of polysaccharide fractions are known in the literature, far fewer of these investigations have focused on CTH of lignin [17]. Rinaldi and coworkers have investigated Raney Ni for CTH of lignin-derived phenols [24]. They found that the catalyst was particularly active for HDO of phenolic compounds. But at the same time, they demonstrated that the catalyst simultaneously affords ring saturation products. This reactivity is undesirable to produce aromatic chemicals, but is particularly attractive if the target of conversion is a saturated fuel mixture. In contrast, Song et al. demonstrated that Ni/C catalysts could catalyze CTH of phenolic lignin monomers derived from birch wood lignin to provide partially deoxygenated products that retain their aromatic character [11]. Recently, Jae and coworkers demonstrated that RuRe/C catalysts are effective for HDO of guaiacol [25]. They concluded that the alloy of Re and Ru in the catalyst enhances reactivity, but also noted that the major product is ring-saturated cyclohexanol.

Boron-containing metal alloys have been the subject of numerous studies given their interesting mechanical, electronic, and catalytic properties [26,27]. B-containing alloys of FeNi have been used for the liquid-phase catalytic hydrogenation of *p*-chloronitrobenzene [28]. Moreover, B-containing alloys of CoMo [29], NiMo [30,31], and LaNiW [32] have been investigated for HDO of phenolic compounds using high-pressure H_2 gas. In addition, NiB generated within the cellular structure of milled wood powders has been shown to be an effective and selective lignin hydrogenolysis catalyst [33]. However, these catalysts have not been investigated as catalytic transfer hydrogenolysis mediators, even though they display a propensity for mediating reductive transformations, including HDO reactions of lignin and lignin model compounds.

Here, we report on the ability of B-containing FeNi nano alloys to mediate catalytic transfer hydrogenolysis (CTH) reactions in supercritical ethanol (sc-EtOH). We have produced the alloyed and the monometallic materials by facile chemical reduction reactions using $NaBH_4$, and we reveal the amorphous nature of the materials using x-ray diffractometry (XRD) and scanning transmission electron microscopy (STEM). We use energy-dispersive x-ray spectroscopy (EDS) to confirm the alloyed nature of the bimetallic species. We note the superior selectivity for the complete deoxygenation of acetophenone to ethylbenzene in supercritical ethanol using the alloyed material instead of the constituent monometallic materials. Finally, we apply CTH in sc-EtOH to organosolv lignin from *Populus deltoides* (hybrid poplar) using the alloyed material to afford partially deoxygenated, depolymerized products. We monitor changes in molecular weight of the lignin before and after catalysis using gel permeation chromatography (GPC), and we identify some deoxygenated monomeric products using GC/MS. We also use ^1H-^{13}C HSQC NMR spectroscopy to demonstrate the utility of the catalyst species to deoxygenate aliphatic hydroxyl and carbonyl groups in the presence of unsaturated C=C bonds and aromatic hydroxyl groups in biorefinery-relevant lignin. Taken together, these results demonstrate the utility of the combination of an earth-abundant catalyst and a biomass-derived solvent to valorize lignin without the addition of external hydrogen.

2. Materials and methods

2.1. Catalyst preparation

All reagents were obtained from commercial vendors and were used as received. The alloy catalysts were prepared using a modified synthesis method reported by Nie et al. [34]. To prepare B-containing FeNi nano alloys, 0.3 M aqueous solutions of $NiCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ were prepared, and 20 mL of each were mixed by magnetic stirring at 300 rpm to obtain equimolar ratio of Fe^{3+} and Ni^{2+} ions. The solution was equilibrated at 75 °C and then 150 mL of freshly prepared 0.2 M aqueous solution of $NaBH_4$ was added dropwise. To prepare B-containing Fe and Ni catalysts, the volume of $NaBH_4$ was adjusted so that the metal ions (Fe^{3+} and Ni^{2+}) are reduced to their metallic states (Fe and Ni). The resulting suspension was filtered and the black precipitate washed with copious amount of deionized water. The precipitate was dried in a vacuum oven at 60 °C for 2 h before grinding into a fine powder using an agate mortar and pestle.

2.2. Catalyst characterization

XRD was performed using a Panalytical Empyrean diffractometer with a Cu K-alpha 1 (high resolution) source (λ = 0.15406 nm) using a voltage of 45 kV and a current of 40 mA. STEM-EDS was performed using a Tecnai Osiris scanning transmission electron microscope operating at 200 kV with a probe current on the order of 1.5 nA. The instrument is equipped with a SuperX EDS system which is composed of four windowless solid state detectors that allow for light element detection down to and including boron. Inductively-coupled plasma optical emission spectroscopy (ICP-OES) measurements were performed on an Optima 7300 DV spectrometer from PerkinElmer.

2.3. Extraction of lignin from hybrid poplar using an organosolv process

The biomass was fractionated using a method reported by Bozell and coworkers [14]. Hybrid poplar chips (~660 g) were loaded in a flow-through reactor and impregnated with a 16/34/50 wt% solution of methyl isobutyl ketone, ethanol, and water, respectively, with sufficient sulfuric acid to make a 0.05 M solution. The reactor was electrically heated to 140 °C while fractionation solution was pumped through the reactor for 2 h at a rate sufficient to generate an ultimate solvent to biomass ratio of 14:1. After 2 h, all the liquor was collected and NaCl (15 g per 100 mL) was added to induce an aqueous-organic phase separation. The organic phase was washed with water (2 × 30% v/v) and concentrated. The resulting material was triturated with diethyl ether (5 × 50 mL), suspended in water (5% solids loading), and stirred overnight to afford a brown solid that was filtered and dried overnight in a vacuum oven at 80 °C.

2.4. Catalytic experiments

2.4.1. Catalytic transfer hydrogenolysis (CTH) of acetophenone

A stock solution containing acetophenone (1.0 mL, 8.6 mmol) and naphthalene (1.0 mL, 3.4 mmol) in absolute ethanol (8.0 mL) was prepared (10 mL total volume). A micro reactor that consists of a 0.5” MNPT stainless steel pipe fitting (Swagelok, P/N: SS-8-HN) and a pair of 0.5” FNPT stainless steel pipe caps (Swagelok, P/N: SS-8-CP) was charged with 10 mg catalyst and 1.0 mL of the above stock solution.