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Efficient depolymerization of lignin in supercritical ethanol by a combination of metal and base catalysts

Q1 Susan Olivia Limarta[a,b], Jeong-Myeong Ha[a,b], Young-Kwon Park[c], Hyunjoo Lee[a,b], Dong Jin Suh[a,b], Jungho Jae[a,b,*]

[a] Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea
[b] Division of Energy & Environment Technology, KIST School, Korea University of Science and Technology, Seoul 02792, Republic of Korea
[c] School of Environmental Engineering, University of Seoul, Seoul 02504, Republic of Korea

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ABSTRACT

This study investigates the use of combination of metal and solid-base catalysts for effective depolymerization of lignin into monophenol-rich bio-oil in supercritical ethanol through a synergy of base-catalyzed solvolysis and metal-catalyzed hydrogenolysis. The results showed that a combined catalyst of Ru/C and MgO/ZrO_2 resulted in a significant decrease in the molecular weight of bio-oil, an increase in the yield of phenolic monomers, and the improved deoxygenation degree of bio-oil compared to the single catalyst condition. The synergic role of metal and base catalysts during lignin depolymerization was examined through comprehensive analysis of reaction products.

Introduction

Lignocellulosic biomass is being investigated worldwide as a sustainable liquid fuel feedstock owing to its abundance, low cost, and carbon neutrality [1]. The major components of lignocellulose are carbohydrate polymers (hemicellulose and cellulose) and an aromatic polymer (lignin), and their distributions are typically 70–90 and 10–30 wt%, respectively. While the technologies for the conversion of the carbohydrate portion of lignocellulose into transportation fuels (e.g., bioethanol) are commercially viable, an efficient conversion technology for lignin has yet to be developed [2–4]. Lignin is a randomly cross-linked polymer of phenylpropane monomers, including *p*-coumaryl, coniferyl, and sinapyl alcohol, bonded by many different linkages (e.g., β-*O*-4, α-*O*-4, 4-*O*-5, β-5, 5-5) [2]. Although lignin is a promising feedstock for the production of fossil-fuel-like aromatic compounds, its structure is highly recalcitrant toward chemical and biological degradation, making the efficient conversion to aromatic chemicals and fuels difficult.

To date, various thermochemical processes such as pyrolysis [5–9], liquefaction [10–13], hydrolysis/solvolysis [14–16], and hydrogenolysis/hydrocracking [17–23] have been explored for the effective depolymerization of lignin into a liquid fuel called bio-oil. Pyrolysis is a simple and economical process for the depolymerization of lignin. However, the pyrolytic degradation of lignin involves a free-radical reaction pathway such that the product distribution is uncontrollable, forming a large amount of solid char by random repolymerization of the radicals [7]. For the hydrolysis/solvolysis of lignin, lignin is depolymerized through the hydrolytic/solvolytic cleavage of the aryl-alkyl ether bonds in lignin in the presence of an acid or base catalyst (preferably a base). Base-catalyzed hydrolysis (e.g., NaOH, KOH) has been shown to be effective at depolymerizing lignin into smaller products such as phenolic monomers, but phenolic monomers are highly reactive, undergoing rapid repolymerization into oligomers or char [14]. Therefore, the amount of obtainable bio-oil containing phenolic monomers is limited by the concomitant polymerization reaction.

The reductive depolymerization of lignin has been studied most extensively in recent years due to its effectiveness for the production of high-yield bio-oil, which contains large amounts of phenolic monomers. In the presence of hydrogen gas and supported metal catalysts, the aryl-alkyl ether bonds in lignin can be selectively cleaved via hydrogenolysis, producing phenolic monomers and oligomers. Alcohols such as ethanol and 2-propanol are commonly employed as a solvent for the hydrogenolysis of lignin due to their high solubility of lignin and their ability to donate hydrogen. For instance, Kim et al. reported that

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Q2 [*] Corresponding author at: Clean Energy Research Center, Korea Institute of Science and Technology, Seoul 02792, Republic of Korea. Fax: +82 2 958 5209.
E-mail addresses: jjae@kist.re.kr, john.jjae@gmail.com (J. Jae).

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soda lignin can be depolymerized to a phenolic-rich bio-oil (~10 wt% of phenolic monomers) at a high yield of ~77 wt% over noble metal catalysts (Pt/C, Pd/C, and Ru/C) in supercritical ethanol [18]. Kloekhorst et al. studied the reductive depolymerization of Alcell® lignin over Ru/C in 2-propanol/formic acid mixtures (1:1 mass ratio) as a solvent and a hydrogen donor at 400 °C [19]. Bio-oil was obtained at a yield of 71 wt% with a high content of phenolic monomers (~21.7 wt%), though the use of expensive solvent-cum-reactant (i.e., formic acid) may not be economical. In addition to noble metal catalysts, non-noble metal-based catalysts (e.g., Ni/C, α-MoC_{1-x}/AC, W_2C/AC, $CuMgAlO_x$) have also been reported to be active for the hydrogenolysis of lignin in methanol or ethanol as a solvent [17,24–26].

In order to enhance the lignin depolymerization efficiency and maximize the production of monomeric phenols, combinations of supported metal catalysts with acid or base catalysts such as Ru/C-NaOH [27], Ni/ZSM-5-NaOH [28], Pd/C-$CrCl_3$ [29], and Pd/C-$ZnCl_2$ [30] have also been explored. In general, the combined catalyst systems greatly improved the extent of lignin depolymerization and the yield of phenolic monomers due to the synergistic effect between the metal (for hydrogenolysis) and acid-base sites (for hydrolysis). However, the use of a homogeneous catalyst such as NaOH and $CrCl_3$ is not desirable for practical applications due to the separation/recycling problem. Recently, Kim et al. showed that the use of noble metal loaded on acidic support (i.e., Ru/H-Beta zeolite) for catalytic depolymerization of empty fruit bunch (EFB)-derived organosolv lignin resulted in the high-yield production of phenolic monomers (~16.5%) and a 63% decrease in the molecular weight of lignin due to the synergic effect of the metal and solid acid [20]. On the other hand, the synergy of metal and solid-base for catalytic depolymerization of lignin was rarely investigated despite the high depolymeriztaion activity of solid-base catalysts such as Na-ZrO_2 [31].

In this work, we investigate the combination of supported metal and solid-base catalysts for the effective depolymerization of kraft lignin into monophenol-rich bio-oil. Ru/C was selected as the supported metal catalyst owing to its high activity for lignin hydrogenolysis. For solid-base catalysts, MgO supported on various support materials (i.e., carbon, Al_2O_3, ZrO_2) were prepared and their physicochemical properties were characterized by XRD, BET, CO_2- and NH_3-TPD. Lignin depolymerization over Ru/C, supported MgO catalysts, and their physical mixtures was conducted, and the changes in the product yields and bio-oil properties (e.g., molecular weight, aromatic monomer distribution, O/C and H/C atomic ratio) were examined in detail in an effort to determine the synergic role of the metal and basic sites during lignin depolymerization. The effects of reaction were also investigated to further improve the lignin depolymerization efficiency with a combined catalyst system (i.e., Ru/C-MgO/ZrO_2).

Material and methods

Materials

The kraft lignin used in this study was purchased from Sigma–Aldrich (CAS-370959). Organosolv lignin was isolated from pinewood sawdust using the modified organosolv process. In brief, pinewood sawdust (1 kg) was treated with the ethanol-water mixture (0.5 L, 66 wt% ethanol) and aqueous sulfuric acid solution (15 mM) at 170 °C for 1 h and the organosolv liquor was obtained by filtration. The lignin sample was dried at 105 °C for 3 h before reaction. Ethanol and acetone (ACS reagent grade) were provided by Daejung Chemicals (South Korea). The catalysts, supports, and metal precursors were purchased from commercial suppliers: activated carbon, 5 wt% Ru/C, $Ru(NO)(NO_3)_3$ and $Mg(NO_3)_2\cdot 6H_2O$ (Sigma–Aldrich, South Korea), Al_2O_3 and ZrO_2 (Alfa Aesar, South Korea). For GPC analysis, HPLC grade tetrahydrofuran (THF) was provided by Alfa Aesar (South Korea).

Proximate and ultimate analyses of lignin feedstock

Proximate analysis was conducted using a TA instruments Q500 Thermogravimetric Analyzer (TGA) in order to obtain the chemical composition of lignin samples (i.e., moisture (M), volatile matter (VM), fixed carbon (FC), and ash). The samples were initially heated up to 110 °C with a ramping rate of 20 °C/min in flowing N_2 (flow rate: 50 cm^3/min) and then held isothermally for 15 min to measure the weight loss for water removal (moisture content). The heating process was continued under N_2 flow to 950 °C with a ramping rate of 20 °C/min to measure the weight loss for volatile matter. On other hand, to determine ash content, the samples were heated up to 950 °C with a ramping rate of 20 °C/min in flowing air and then held isothermally for 15 min. The residue remaining after combustion represents ash content.

The contents of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) in the lignin samples were measured by using a Flash 2000 series CHNSO analyzer (Thermo Scientific, MA, USA) with multi-separation column (PTFE, 2 m × 6 mm × 5 mm) and flame ionization detector (FID). Oxygen (O) content was measured by using a Fisons-EA-1108 analyzer (Thermo Scientific, MA, USA) with oxygen separation column (SS, 1 m × 6 mm × 5 mm) and FID.

Catalyst preparation

MgO/ZrO_2 was synthesized by an incipient wetness impregnation method. ZrO_2 was initially calcined in static air at 400 °C for 5 h. $Mg(NO_3)_2.6H_2O$ (3.53 g) was dissolved in distilled water (3.4 mL) and was then slowly impregnated into the calcined ZrO_2 (5 g). After impregnation, the sample was kept at room temperature for 1 h followed by drying at 120 °C for 12 h. The same procedure was used for MgO/C and MgO/Al_2O_3. All of the MgO loaded on different supports were treated at 600 °C for 3 h with a heating rate of 5 °C/min under N_2 flow. 5 wt% Ru/MgO/ZrO_2 was also prepared by successive impregnation of calcined MgO/ZrO_2 with $Ru(NO)(NO_3)_3$. Before reaction, Ru/C and Ru/MgO/ZrO_2 were reduced at 300 °C for 3 h in a flowing mixture of H_2 (5%) and Ar (95%) followed by passivation at room temperature for 2 h in a flowing mixture of O_2 (0.5%) and N_2 (99.5%).

Catalyst characterization

Powdered X-ray diffraction (XRD) was performed on a Shimadzu Lab XRD 6000 with CuKα radiation ($\lambda = 1.5418$ Å). N_2-physisorption measurements were performed in a BELSORP-mini II (BEL Japan, Inc.) at 77 K to determine Brunauer–Emmett–Teller (BET) surface areas and pore volumes of the catalysts. Temperature programmed desorption of ammonia (NH_3-TPD) was conducted by using a BELCAT-B temperature programming unit (BELCAT, Osaka, Japan) coupled with thermal conductivity detector (TCD) and mass spectrometer to determine the acid site density of the catalysts. Before TPD measurements, the sample was pretreated at 350 °C for 15 min in flowing He followed by exposure to a 5% NH_3/He gas at 100 °C for 30 min. The TPD of ammonia was then monitored at a temperature ranging from 100 to 850 °C. The same instrument was used for temperature programmed desorption of carbon dioxide (CO_2-TPD) to determine the basic site density of the catalysts. Before measurements, the sample was pretreated at 600 °C for 1 h in flowing He followed by exposure to the pulses of 4.98% CO_2/He at 40 °C for 30 min. CO chemisorption was performed using a BELCAT-M (BEL Japan, Inc.) equipped with thermal conductivity detector (TCD). Prior to measurement, the catalyst

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