Hydrogenation of Lignin-derived Phenolic Compound Eugenol over NiRu-HT-Type Materials

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ABSTRACT: Sustainable production of fine chemicals and fuels from renewable energy resources are important processes in the current scenario of the energy crisis. In this study, we have reported complete hydrogenation of eugenol, which is an important biomass-derived molecule, using ruthenium-containing nickel hydrotalcite (NiRu-HT)-type materials and isopropyl alcohol as a solvent. A series of group VIII metals containing bimetallic Ni-HT-type materials were synthesized, characterized, and demonstrated to participate in eugenol conversion and among which Ni-Ru-HT was found to give the highest selectivity towards alkyl cyclohexanol. The reaction conditions, including reaction temperature, hydrogen pressure, and Ni/Ru ratio, were optimized. Based on the results, it can be concluded that eugenol was first hydrogenated to 4-propyl guaiacol and then undergo simultaneous demethoxylation and aromatic ring hydrogenation to form 4-propylcyclohexanol. Moreover, various lignin-derived phenolic compounds can be efficiently converted into alkyl cyclohexanols and aromatic compound into alkyl cyclohexane. The *in-situ* formation of metallic ruthenium on the surface of NiRu-HT as evident from TPR and TEM analyses and are responsible for observed high yield of ring hydrogenated product of eugenol (i.e., 4-propylcyclohexanol).

1. INTRODUCTION

Fossil fuel depletion and increasing energy demands have encouraged researchers to focus on the development of new sustainable technologies to produce fuels and chemicals from renewable energy resources[1–3]. Among the various renewable energy resources, biomass is one of the carbonaceous energy resources, which appears to be promising for the production of transportation fuels and platform chemicals[3]. Biomass can be defined as a biological organic matter derived from living or non-living organisms. Agricultural, forestry crops and residues, animal residues, municipal solid and sewage waste materials, and wood from various sources are the major sources of biomass. Non-edible plant-derived biomass is generally called lignocellulosic biomass. Due to its low cost and high abundance, lignocellulosic biomasses are drawing worldwide attention as an alternative feedstock to fossil fuels. Lignocellulosic biomass consists of 40–50% cellulose (polysaccharide consisting of glucose units), 25–30% hemicellulose (heteropolymer of C_5 and C_6 sugars), and 10–25% lignin (aromatic polymer) with some minor components, such as nutrients, proteins, and wax (1–10%) [1–10]. The structure of lignin is formed via oxidative coupling reactions of three different phenylpropane building blocks, including *p*-coumaryl, coniferyl, and sinapyl alcohols (Scheme 1). Due to its complexity, lignin depolymerization and upgrade of corresponding monomers for the target compound production is significantly important. Eugenol is the most promising model compound of phenolic fractions of lignocellulosic bio-oil derived by lignin pyrolysis (Scheme 1).[4-6,12] The importance of this molecule is that it consists of several key functional groups, including phenyl, hydroxyl, methoxy, and allyl groups, which are part of all of the three main constituents of lignin[4, 6, 11–13]. The bio-oil produced by pyrolysis of lignin cannot be directly used as a transportation fuel as it contains a large number of oxy functional groups and has to be upgraded. Catalytic methods are used to reduce oxygen content and improve hydrogen/carbon ratios. Catalytic hydrogenation, hydrodeoxygenation (HDO), and isomerization are the most promising routes for the upgrade of lignin-derived bio-oils to biofuel and fine chemicals. In this regard, eugenol is chosen as a lignin monomeric model compound having olefin, methoxy, aromatic and hydroxy functionality and is a potential molecule to understand the catalytic behavior.[2] Often most of the transition