



Hydrodeoxygenation of lignin model compounds over a copper chromite catalyst



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ABSTRACT

The hydrodeoxygenation of benzyl alcohol, phenol, anisole, o-cresol, catechol, guaiacol, and vanillyl alcohol were carried out from 150 to 275 °C at 50 bar H₂ with a CuCr₂O₄-CuO catalyst in a decalin solvent. The hydroxymethyl group of benzyl alcohol was found to be highly reactive towards hydrogenolysis to form toluene. Demethoxylation of anisole to form benzene was found to be the primary reaction pathway in contrast to demethylation and transalkylation reactions, which are more prevalent for conventional hydrotreating catalysts. The hydroxyl group of phenol strongly activated the aromatic ring towards hydrogenation forming cyclohexanol which was subsequently dehydrated and hydrogenated to form cyclohexane. Reaction networks of increasing complexity were devised for the major functional groups and integrated to describe the most complex molecule studied, vanillyl alcohol.

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1. Introduction

The utilization of biomass to produce fuels and chemicals is a topic of increasing importance as petroleum prices rise and reserves diminish. Numerous technologies are under investigation to utilize the various components of biomass: cellulose, hemicellulose and lignin. A key challenge in the chemical and thermal conversion of biomass is the reduction of oxygen content to produce fuels and chemicals that are compatible with conventional petroleum-based products. Hydrodeoxygenation (HDO) is a promising upgrading technology that has gained considerable attention in recent years due to the high oxygen content of biomass derived feedstocks, especially in the context of pyrolysis oil upgrading [1–5]. Of particular importance is the minimization of hydrogen consumption by developing catalysts that can perform HDO while minimizing the hydrogenation of unsaturated phenolic and furanic species that are common in biorenewable feedstocks.

Conventional hydrotreating processes have focused primarily on hydrodesulphurization (HDS) and hydrodenitrogenation (HDN) because oxygen content in crude oil is very low and does not pose the same environment issues as burning S- or N-containing fuels [1]. Many studies of HDO have focused on the phenolic components of bio-oil which represent a considerable portion of the

liquid product from fast pyrolysis [6]. The lignin-derived components of biomass are commonly used as model compounds for HDO because they possess the aromaticity that is important to maintain to minimize hydrogen consumption [2]. Furthermore, phenolic compounds contain several oxygen functionalities including hydroxyl groups bound to aromatic and aliphatic carbons and methoxy groups that all have different HDO reaction pathways and susceptibilities [7].

Numerous HDO studies have investigated the use of conventional hydrotreating catalysts consisting of sulphided NiMo–Al₂O₃ or CoMo–Al₂O₃ for bio-oil upgrading [8–32]. Both catalysts have shown to be effective at HDO, where NiMo–Al₂O₃ favors hydrogenated products and CoMo–Al₂O₃ favors aromatic products. However, there are several concerns with using sulphided catalysts in HDO such as the loss of the sulphided phase over the course of processing and the introduction of sulphur into the product stream [11,13,15,21,30,33,34]. Some researchers have proposed co-feeding H₂S to maintain the sulphided phase; however, H₂S competitively adsorbs with oxygenated compounds and proportionally decreases the selectivity towards hydrogenolysis, which lowers the production of aromatics. Coking has also been shown to be a significant issue with the conventional hydrotreating catalysts, which has been attributed to the acidity of the support [11,16,17,27,35,36].

Alternatives to the sulphided molybdenum hydrotreating catalysts have been investigated in more recent years [33–46]. Noble metals have shown high activities in HDO; however, aromatic saturation is observed unless high temperatures and atmospheric

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