



# Revealing the factors determining the selectivity of guaiacol HDO reaction pathways using ZrP-supported Co and Ni catalysts



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## ARTICLE INFO

### Article history:

Received 6 March 2019

Revised 24 May 2019

Accepted 15 July 2019

Available online 8 August 2019

### Keywords:

Guaiacol

Hydrodeoxygenation

Reaction pathway

Co/ZrP

Ni/ZrP

## ABSTRACT

Guaiacol, a primary chemical derived from lignin, is still an attractive candidate as a cyclical carbon source in the petroleum industry. This work newly introduced Co/ZrP and Ni/ZrP catalysts and examined their activity for guaiacol hydrodeoxygenation (HDO) in a batch reactor at 573 K and under 70 bar of H<sub>2</sub>. Their catalytic, surface and textural properties were investigated by XRD, N<sub>2</sub> adsorption-desorption, H<sub>2</sub>-TPR, H<sub>2</sub>-TPD, NH<sub>3</sub>-TPD, HAADF-STEM and H<sub>2</sub>-chemisorption. In addition, the overall reaction pathways of guaiacol to cyclohexane on Co/ZrP and Ni/ZrP were proposed. Guaiacol was converted to cyclohexane through two different pathways via two major intermediates: phenol (demethoxylation, PHE route) and 2-methoxycyclohexanol (hydrogenation, 2-M route). Co/ZrP preferred the PHE-route, while Ni/ZrP dominantly favored the 2-M-route, which resulted in a high cyclohexane yield when using Co/ZrP (76%). In this study, an 'intrinsic H<sub>2</sub> supply' was determined to be the main factor for selecting the reaction pathway. Co/ZrP, with a low intrinsic H<sub>2</sub> supply capacity, promoted a less H<sub>2</sub>-consuming pathway (PHE route), and Ni/ZrP, with a high intrinsic H<sub>2</sub> supply, favored the more H<sub>2</sub>-consuming 2-M route. Likewise, lowering the H<sub>2</sub> pressure (from 70 to 40 bar) could promote the PHE route and increase cyclohexane production (80%). However, the opposite trend was observed when the reaction temperature was reduced from 573 K to 523 K. For both Co/ZrP and Ni/ZrP catalysts, the production of PHE significantly decreased, while the same yield of 2-M was almost maintained. Thus, the pathway preference of Co/ZrP was reversed to the 2-M-route. Guaiacol HDO pathway preference over Co/ZrP and Ni/ZrP catalysts was characterized and the reaction conditions were investigated in this study, which could provide a guideline for effective ways to produce desired chemicals from guaiacol using Co/ZrP and Ni/ZrP.

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## 1. Introduction

Global energy consumption is steadily increasing while conventional petroleum is being depleted and is causing a serious energy crisis [1–3]. Renewable energy resources (e.g., biomass, solar and wind) can be competitive alternatives for the insufficient energy supply. Biomass, a sustainable and carbon recyclable resource, has two major potential uses: biofuel and chemical resource (carbon source) [1,2,4–14]. Biofuel derived from biomass can be used as a transportation fuel owing to the viability of large-scale, sustainable manufacturing [1,2,4–7,15–17]. However, there have already been various trials to replace conventional fuel with other renewable energy resources (e.g., solar, wind and hydrogen) [18–

22]. Thus, more importantly, a role as a carbon feedstock for the chemical industry makes biomass an irreplaceable resource [8–11]. In other words, only the carbon based resources can cover the demands for carbon sources that will continue to be needed.

Lignin is one of the three major components of wood and is gaining popularity because it has the potential to become a green source of aromatic compounds without affecting food prices [3,14,16,23,24]. When exploiting lignin, its excess oxygen content (up to 50 wt%) is typically decreased to produce chemicals or high-quality biofuels [1,4,25–27]. Thus, hydrodeoxygenation (HDO) is a key reaction in utilizing lignin-derived compounds via pyrolysis [28–31]. Furthermore, the conversion from biomass to chemicals via proper deoxygenation is thermodynamically more advantageous than that from conventional petroleum via partial oxidation [32].

To select a model compound for lignin, its chemical structure with intricate linkages has been studied and characterized

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