

## PRODUCTION OF CYCLOHEXANOL FROM METHOXYPHENOLS OVER RUTHENIUM CATALYST COMBINED WITH BASE

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Partial hydrodeoxygenation of biomass-related compounds is a key reaction in biorefinery. Methoxyphenols such as guaiacol are important bio-related compounds as components of bio-oil and as model compounds of lignin-derived monomers. Hydrodeoxygenation of guaiacol has been studied by several research groups, and typical catalysts used are conventional hydrotreating catalysts such as CoMoS and NiMoS. Although there are some catalytic systems for the production of hydrocarbons and methanol or for the production of phenol or cyclohexanol with good yields, selective formation of both cyclohexanol/phenol and methanol has not been well established. In this study, hydrodeoxygenation of guaiacol was carried out using noble metal catalyst with some additives.

Ruthenium catalyst was most effective among various C-supported noble metal catalysts for the production of cyclohexanol from guaiacol. The main by-products were cyclohexane and 2-methoxycyclohexanol. Addition of base such as MgO suppressed unselective C-O dissociation and increased the cyclohexanol yield. High reaction temperature and low hydrogen pressure were preferable for cyclohexanol formation. Around 80% yield of cyclohexanol and methanol was obtained in the optimized reaction conditions (guaiacol 0.5 g, water 10 g, Ru/C 50 mg, MgO 50 mg, H<sub>2</sub> 1.5 MPa, 433 K, 2 h). 3-Methoxyphenol and 2,6-dimethoxyphenol were also converted into cyclohexanol in good ( $\geq 70\%$ ) yield over Ru/C catalyst combined with MgO. 4-Methoxyphenol was also converted to cyclohexanol although the yield was lower (55%). Anisole and 1,2-dimethoxybenzene were not efficiently converted to cyclohexanol, and the main product was methoxycyclohexane and 1,2-dimethoxycyclohexane, respectively.

Based on the reaction results of related substrates such as catechol, 2-methoxycyclohexanol and phenol, we proposed one reaction mechanism: demethoxylation of guaiacol to phenol followed by hydrogenation to cyclohexanol. One route for unselective C-O dissociation is acid-catalyzed dehydration of alcohols to alkenes followed by hydrogenation, and this reaction might be suppressed by base. Demethoxylation of guaiacol can proceed via partial hydrogenation of guaiacol to dihydroguaiacol and decomposition of dihydroguaiacol to phenol and methanol. Further hydrogenation of dihydroguaiacol gives 2-methoxycyclohexanol, and this side-reaction is promoted by high H<sub>2</sub> pressure. High reaction temperature increases the rate of decomposition of dihydroguaiacol in comparison with hydrogenation to 2-methoxycyclohexanol.