Aerobic Oxidation of Veratryl Alcohol to Veratraldehyde with Heterogeneous Ruthenium Catalysts

Lignin is a complex polymeric molecule constituting various linkages between aromatic moieties. Typically, the β-O-4 linkage accounts for more than half of the linkage structures present in lignin. The current study focuses on the oxidative transformation of veratryl alcohol (VA)—a compound that can be formed by cleavage of β-O-4 linkages in lignin—to veratraldehyde (VAld) with air using ruthenium supported on γ-alumina or silica as catalyst with water or methanol as solvent in a batch reactor. Ru/Al₂O₃, prepared with ruthenium(IV)oxide hydrate showed superior catalytic activity, yielding 89 % VAld in water at 160 °C with 5 bar air pressure after 8 h of reaction. Prolonged reaction time led to significant formation of the decarbonylated product veratrol from VAld. When the reaction was completed under 20 bars of argon in methanol instead of water, the methyl ether of VA (i.e. 1,2-dimethoxy-4-(methoxymethyl)benzene) prevailed, indicating that methanol protected the hydroxyl group in VA from being oxidized to VAld. Catalysts containing alternative transition metals (Mn, Co, Cu and Ag) supported on Al₂O₃ gave significantly lower activities compared to Ru/Al₂O₃ under identical reaction conditions. The Ru/Al₂O₃ catalyst was reused in three consecutive reaction runs in water, but a decrease in VAld yield was obtained after the third cycle possibly due to leaching of Ru from the support.