# Catalytic upgrading of biomass-derived platform chemicals via hydrodeoxygenation/hydrogenolysis by metal catalyst

**X. B. Ma,* X. F. Wang, W. Zhou, H. Wang, Y.J. Zhao**

*School of Chemical Engineering & Technology, Tianjin University, Tianjin 300350, China*
*Corresponding author: xbma@tju.edu.cn

## Abstract

As a renewable carbon resource, biomass (including vegetable oils or animal fat, and lignocellulosic biomass) has attracted much attention for its transformation to fuels and chemicals. Glycerol is by-produced during the synthesis of biodiesel from renewable oils and fats, while lignin is underutilized in the refinery processes of bioethanol production from lignocellulose, especially cellulose and hemicellulose[1-2]. Catalytic hydrodeoxygenation or hydrogenolysis is regarded as one of the most efficient approaches for upgrading the biomass-derived platform chemicals into high valued products[3].

Dihydric alcohol (including 1,2-propanediol and 1,3-propanediol) is a series of useful C3 products derived from glycerol[4]. Cu based catalysts were widely reported for the high efficiency of 1,2-propanediol production, while WOx based catalysts were reported for high selectivity towards 1,3-propanediol[5-7]. Our work established the effect of active structure, metal–oxide interaction, hydrogen spillover and acid properties on the hydrogenolysis of glycerol into 1,3-propanediol over the Pt-WOx system, and revealed the reaction mechanism[8-11]. The hydrogen spillover played a crucial role for enhancing glycerol hydrogenolysis activity on WOx-rich catalysts, which was attributed to the controllable crystal structure of Pt(111) and metal–oxide interaction. Moreover, the medium polymerization degree of WOx domains was proved to be more efficient for the production of 1,3-propanediol. When the active structure Pt-(WOx)n-H with medium polymeric WOx domains and strong Brönsted acid sites was formed, the formation rate of 1,3-PDO was much improved.

Arene is a typical and valuable aromatic compound produced from lignin. Metal catalysts (such as Ni, Pt, Rh, etc.) often lead to a saturation of benzene rings, which decreases the arene selectivity. Considering high selectivity of Cu catalysts for hydrogenation of carbonyl compounds and alcoholic compounds, we developed Cu-based catalysts for the selective hydrodeoxygenation of lignin-derived anisole into arene[12-14]. The moderate modification of metal oxides (such as ReOx and MnOx) contributed to the optimization of the active Cu surface and the construction of synergistic sites between metal Cu and oxophilic metal center or oxygen vacancies. The direct deoxygenation activity of anisole to arene was significantly enhanced on the uniform synergistic sites, where the adsorption of $C_{Ar}$-O bond and benzene rings were more controllable. Furthermore, the alkali species (Na, K, Rb, and Cs) as electronic promoters over Cu sites, the electron-rich Cu sites efficiently inhibited the saturation of benzene rings due to the formation of an electron-gap between benzene rings and Cu, and much higher arene selectivity (~ 83%) was obtained on Cs/Cu@NS-$SiO_2$.

In summary, highly efficient metal (e.g., Pt, Cu) catalysts have been developed for the conversion of glycerol and lignin-derived anisole, with comprehensive mechanisms revealed, providing insights for further design of catalyst. The work are expected to promote the development of biodiesel manufacture and lignin upgrading.

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