Selective hydrogenolysis of cellulose and its derivatives to chemicals: catalytic functions and reaction pathways

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Cellulose is the most abundant source of biomass on earth. Cellulose and its derivatives, such as glucose, sorbitol and 5-hydroxymethyl furfural, provide renewable alternatives to fossil fuels for synthesis of fuels and chemicals. In this work, we report our recent progress in catalytic conversion of cellulose and its derivatives into alcohols and carboxylic acids, focusing on our understanding on the requirements for catalytic functions and reaction pathways.

Supported Ru clusters efficiently catalyzed the selective hydrogenolysis of sorbitol to ethylene glycol and propylene glycol. The sorbitol hydrogenolysis requires bi-functional requirements and involves the competitive Ru- and base-catalyzed reactions of ketose or aldose intermediates, derived primarily from kinetically-relevant sorbitol dehydrogenation. This dehydrogenation step most likely proceeds by preferential activation of its C(5)-H bond on the Ru surfaces. Glycerol hydrogenolysis turnover rates (normalized per surface Pd atom measured by H_2 chemisorption) and propylene glycol selectivity on the PdZn/m-ZrO_2 catalysts depend sensitively on their Zn/Pd molar ratios. The kinetically-relevant step of glycerol hydrogenolysis involves the α-C-H cleavage in 2,3-dihydroxypropanoxide intermediate to glyceraldehyde on PdZn alloys and Pd. The transition state of α-C-H cleavage is more stable, due to the stronger oxophilicity of Zn, on PdZn alloys than on Pd, which thus facilitates α-C-H cleavage of the Zn-bound intermediate by adjacent Pd on PdZn alloys.

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