Abstract

Technologies for the processing of lignocellulosic biomass into fuels and chemicals are generally focused on selective chemical transformation of the three different types of constituents; cellulose, hemicellulose and lignin. In this regard, heterogeneous catalytic reactions are employed to defunctionalize and upgrade the platform molecules obtained selectively from these constituents. Herein, systematic studies were performed to deoxygenate and valorize the biomass-derived platform molecules. The selection employed ring-opening, decarboxylation, hydrogenation and hydrodeoxygenation (HDO) reactions carried out on supported metal and oxide catalysts. The platform molecules studied here included an array of cellulose–derived lactones, furans, 2-pyrones and lignin-derived phenolic compounds.

Study on the conversion of lactones (saturated cyclic esters) was focused on understanding the mechanism of ring-opening and decarboxylation reaction. More specifically, oxocarbenium ions were proposed as an intermediate, to play an important role in controlling the rate of ring-opening step. The mechanism of ring-opening and decarboxylation reaction in unsaturated cyclic esters (2-pyrones) formed an interesting case, wherein the reaction in partially saturated 2-pyrones followed a retro-Diels-Alder (rDA) route to selectively yield the desired deoxygenated product. Both solvents and substituents were expected to influence the rDA reaction of partially saturated 2-pyrones, which was studied using density functional theory (DFT) simulations.

An attempt was made to identify a new platform molecule other than the ones listed in the Top-12 list of biobased molecules proposed by the Department of Energy (United States). Towards this, 6-amyl-α-pyrone (6PP) was suggested as a potential platform chemical, which may be obtained directly from the fermentation of waste lignocellulosic biomass. On ring-opening and decarboxylation, 6PP was converted to C₉ linear ketones which are proposed as precursors for jet and diesel range fuels. On hydrogenation, 6PP was converted to δ-decalactone (DDL), which is a food and flavor compound. All of these catalytic transformations of 6PP can be integrated with the upstream fermentation of biomass to form a unique bio- and chemo-catalytic process for providing high value fuels and chemicals.

Towards the development of this integrated fermentation and catalytic process, biogenic impurities (amino acids and protein residues) present in ppm levels (<100 ppm) along with the fermentation-
derived molecules pose a detrimental effect to heterogeneous catalyst stability. Interaction of such impurities with the metal catalyst surface was studied for the first time using DFT simulations. The fundamental knowledge thus developed is expected to open up possibilities of rational design of metal catalyst surface for destabilizing interactions with the biogenic impurities and thereby providing greater stability to the heterogeneous catalyst working in aqueous environment. In this regard a bimetallic alloy of Ni-Au was proposed as a more stable surface for hydrogenation reactions as compared to the bimetallic Pd-Au and monometallic Pd and Ni catalysts.

Catalytic hydrogenation reaction carried out on the Pd catalyst was an interesting case to further explore the influence of catalyst particle size and morphology on the selectivity of a desired product. Phenol hydrogenation reaction on supported and unsupported Pd catalyst was studied as a model reaction, since phenolic compounds are derived from the lignin part of biomass. Detailed mechanistic studies were carried out on Pd (111) and Pd (100) surfaces using DFT calculations to corroborate experimental finding of the collaborating group. Since Pd (111) are the majority (~70% of the surface) sites, high selectivity observed towards the partially hydrogenated product (cyclohexanone) in the experiments is thought to be from the Pd (111) surface. Contrary to this prevalent thought, on using a combined theoretical and experimental approach, Pd (111) surface was demonstrated to selectively produce the completely hydrogenated product, cyclohexanol. Surprisingly, Pd (100), the minority (~25%) sites on the surface, were selectively producing cyclohexanone. These results lead to the development of a comprehensive understanding on facet-dependent selectivity control in phenol hydrogenation on the Pd catalyst.

Final reaction in this sequence was HDO of biomass-derived furan compounds, wherein the synergistic interaction of Zn with the Pd catalyst was studied using DFT simulations. Zn was shown to participate in C-O bond activation step while Pd surface participated in the hydrogenation step. Overall the study covering an array of platform molecules and catalytic reactions is focused on developing a mechanistic understanding with insights into key fundamental challenges and available opportunities on engineering the catalyst surface.