Catalytic Valorization of Lignocellulosic Biomass for the Production of Valuable Chemicals

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Abstract

The rising fuel prices along with the numerous climatic concerns such as global warming, acid rains, melting of glaciers, etc, severely affect the incessant use of fossil reserves. By the year 2040, it is expected that the exponential rise in energy demands will be enhanced significantly by about 28% of its present value. Lignocellulosic biomass (LCB) is an attractive alternative due to its abundancy and its ability to produce a wide range of fuels and chemicals. Considering the availability of LCB in India (~ 750 million tons), LCB conversion to fuels and feedstocks is significant to tackle the burning clean energy issues. LCB consists of complex networks containing cellulose (30-50%), hemicellulose (20-35%), and lignin (15-30%). A wide range of chemicals e.g., sorbitol, xylitol, ethylene glycol, 5-hydroxymethylfurfural, levulinic acid, guaiacol, vanillin, phenols, etc, can be extracted *via* different reactions viz., dehydration, hydrogenation, oxidation, hydrolysis, hydrodeoxygenation, retro-aldol condensation, etc, in the presence of catalysts.

This thesis is focussed on development of efficient catalysts for valorization of all the three components of LCB which will be beneficial for the commercialization of sustainable future bio-based refineries. Investigation of one-pot hydrolytic hydrogenation of cellulose to ethylene glycol and hexitols by a combination of heteropolyacid/ZrO_2 and Ru/C was done. The heterogeneous system produces 26.5% hexitol and 40% ethylene glycol yield. Mechanistically, it was also proved that initial hydrolysis of cellulose to glucose followed by the formation of glycolaldehyde was also accomplished by heteropolyacid/ZrO_2 support. The intermediate glycolaldehyde and glucose was successively reduced to ethylene glycol and hexitols, respectively, by Ru/C. Moreover, prior treatment of cellulose by ball-milling reduces its crystallinity and thus accounts to high conversion to cellulose. In another study, organic-inorganic hybrid metal-free sulfonated porphyrin-based porous organic polymer was synthesized for the production of 5-hydroxymethylfurfurl (HMF) from fructose in water. The research is advantageous and shows high HMF yield of 85% in water, therefore bypassing the use of toxic organic solvents. Incorporation of silica introduces hydrophilicity as well as inter-particle mesopores to enhance interaction and diffusion of bulky substrates like fructose,

resulting in high HMF yield. Acid/base bifunctional organocatalyst was developed for direct conversion of glucose to HMF in water giving a HMF yield of 60% under optimum conditions. A thorough kinetic modelling was also done and the values predicted by the developed model were found to give an excellent fit with the experimental data. Environmentally-friendly deep eutectic solvents (DESs) were also synthesized and applied for the synthesis of HMF. HMF yield of 88% was achieved when the reaction was performed under the microwave irradiation at 140 °C for 30 min in the presence of acetone: water and choline chloride (ChCl): lactic acid (LA) DES. The release of H^+ from the DES was favored due to competing hydrogen bonding interactions between OH group of lactic acid and fructose, which promoted the dehydration of fructose to HMF. Furthermore, DESs have also been utilized for the pretreatment of LCB to extract lignin in high purity without much alteration in its native structure. Under optimum conditions (150 °C, 20 min, ChCl: LA DES), lignin yield of 82% was achieved using microwave heating. A study was also done to show the advantages of Ru-single atoms for one-pot hydrogenation of xylose and glucose to xylitol and sorbitol, respectively. The use of Ru-single atom shows significant advantages over Ru-NPs supported catalysts for the hydrogenation of sugar molecules using hydrogen donor solvents and thus avoiding the use of high-pressure external hydrogen. Under such context, Ru-single atom catalyst enables steady production of xylitol with 95% yield. This research deals a mild protocol to utilize biomass-feedstocks for producing commercially important low-calorie sugars.