For furfural acetalization with alcohols, a three-step reaction mechanism was proposed: (i) alcohol hydroxyl-dehydrogenation (ii) hydrogenation of furfural carbonyl oxygen, and (iii) formation of hemiacetal product as shown in Figure 3(i). Pd (100) exhibited low activation barriers (51.6, 26.7 and 76.2 kJ/mol) compared to Pd (111) surface (78.6, 35.8 and 92.2 kJ/mol) in the presence of ethanol for all three steps which corresponds well with the experimental data. The activation barriers for the above steps were further reduced to 47.8, 23.9 and 64.6 kJ/mol on Pd (100) in the presence of methanol, explaining the experimental high reactivity aided by methanol.

DFT calculations elucidated the role of the hydrogen bonding network between the solvent molecules (Figure-3 (ii)) and adsorbate, enabling proton coupled-electron transfer for accelerated reactions. The explicit treatment of alcohol molecules in our model offers an advantage to study the molecular level details of the solute-solvent interactions and can be easily extended to other reactions involved in biomass conversion.

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Enzymatic synthesis in green chemistry

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When two molecules join hands to form a new molecule, the process is called reaction. Reactions are often assisted by a third molecule called the catalyst and the process being called catalysis. Chemical catalysts have been the chief pillars of many industries from time immemorial. However, chemical catalysis has several shortcomings like extreme working conditions, use of hazardous reagents, and a lack of regulatory control. This has motivated researchers all around the globe to develop sustainable catalysis by exploring biological catalysts, called enzymes, which assist every life process with a high specificity for a given process. Moreover, enzymes are equipped with an element of regulation allowing them to function as and when needed. Research on enzymatic catalysis outside the biological context, for example, under the aegis of "green chemistry", has revealed promiscuity for alternative processes in some enzymes. This has revolutionized catalysis research to focus more and more on engineering enzymes to perform specialized catalysis for the production of certain non-natural compounds of therapeutic or industrial importance. Green chemistry facilitates the economic, safe, and eco-friendly production of valuable compounds. Biocatalysis or enzyme-mediated catalysis is one of the fields my research lab is focused on. We work on one of such enzymes called PARPs or Poly (ADP-ribose) polymerases, which catalyzes the formation of a polymer called poly (ADP-ribose) or PAR in the cells using the substrate NAD+ (Nicotinamide adenine dinucleotide). PAR is a highly negatively charged polymer. We have been working on PARP enzymes to make non-natural PAR-like polymers using non-native substrates. The anionic biopolymers can widely be used for drug delivery, regenerative medicine purpose and several other applications in pharmaceutical and healthcare sector.

Since we have been successful in making the non-natural polymer using PARP enzymes, our next course of action would be to test its applications.

Another enzyme we work on is the plant enzyme strictosidine synthase (STR) which unlike PARP enzymes uses two substrates. Bisubstrate enzymes are common subjects of wide catalysis research because of their shear prevalence in all life forms. STR catalyses the condensation of two molecules, tryptamine and secologanin, into strictosidine – the precursor for several drugs such as reserpine (antihypertension) and vinblastine (anticancer). Promiscuity in STRs for non-native substrates beyond tryptamine and secologanin has been harnessed for the green synthesis of harmicine (antileishmanial and antinociceptive). However, a catalytic outcome with such substrates varies across the STRs from different plant species. We have been working to explore the substrates' binding mechanisms in a variety of STR enzymes to understand their role in the differing catalytic outcomes. The orientation of atoms in molecules, also known as chirality, plays an important role in drug efficacy. Enzymes like STR are exploited to synthesize a molecule with desired chirality in excess, which is a major bottleneck in classical chemical synthesis approaches. Our study helps to engineer the STRs to catalyze reactions with non-cognate substrates. Also, we plan to design STR variants to get products with the desired properties.

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