For instance, our successful synthesis of tert-Alcohols, [11] 3-Selenylindoles,[12] Sulfonated 2H-Chromenes, [13] Fused Sulfenyl Phenanthrenes, and Sulfenyl Spiro Cyclohexa[4.5]trienones[14] relied on sustainable methods (Figure-1). These protocols work under mild reaction conditions at ambient temperature, utilizing constant current electrolysis in an undivided cell without utilizing external oxidants, reductants, or catalysts. We are currently focusing our research on overcoming challenges and optimizing these methods for widespread use in the chemical industry.

In conclusion, electrochemical organic synthesis would pave the way for its widespread adoption and open new possibilities for sustainable and efficient chemical transformations in organic synthesis and its applications across various fields. As research in this field continues, it will likely yield innovative solutions in achieving complex organic compounds with reduced environmental impact.

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Elucidating the facet dependence for solvent-mediated furfural acetalization reaction on Pd nanostructures


1


2

KID: 20230410

Structure-sensitive reactions are well known in heterogeneous catalysis and surface science wherein particle-size and shape-dependent catalytic activity and selectivity control is observed with nanoparticle systems. The size-dependent structure sensitivity arises due to the change in the proportion of the type of surface atoms (viz terrace, corner, or edge) with size. As the size increases, the fraction of terrace sites increases at the expense of edge or corner sites which is reflected in reactivity. Another parameter could be particle morphology, wherein particles with differently exposed facets show different reactivity. In addition to the structural and morphological effects, the performance of a catalyst is strongly affected by solvent properties such as polarity, basicity or proticity; therefore, finding the right solvent for a catalytic reaction is important.

In this context, the structure-sensitive behaviour and solvent effect towards an important reaction for the production of biofuels was investigated in the present study. Furfural dialkyl acetals (FDA) obtained from the acetalization of biomass-derived furfural (Figure-1) are promising biofuels because of their high calorific value and oxidation resistance. Using defined experiments (in collaboration with Dr. C.P. Vinod's Group at NCL Pune) and density functional theory (DFT) simulations, the structure-dependent activity and selectivity for furfural acetalization reaction in the presence of alcohols (methanol, ethanol, propanol and butanol) as solvents were studied over well-defined supported Pd nanostructures (octahedra (111), cubes (100) and spheres (both (111) and (100)) (Figure-2).

FIgure-1: Catalytic route for the production of furfural dialkyl acetals from biomass derived furfural

Pd cubes exhibited high furfural conversion (80%) and acetal selectivity (93%) compared to Pd octahedras (35% and 77%) and Pd Spheres (35% and 77%). Further, when the reaction was carried out in the presence of methanol as solvent highest conversion (90%) and selectivity (100%) for furfural acetalization was obtained over Pd cubes. DFT simulations provided mechanistic insight into furfural acetalization reaction in the presence of alcohol molecules on two different Pd facets (111) and (100).

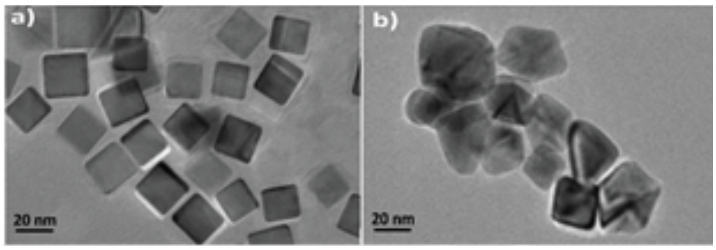

Figure-2: TEM image of (a) Pd cubes (~ 22 nm) and (b) Pd Octahedra (~ 26 nm).

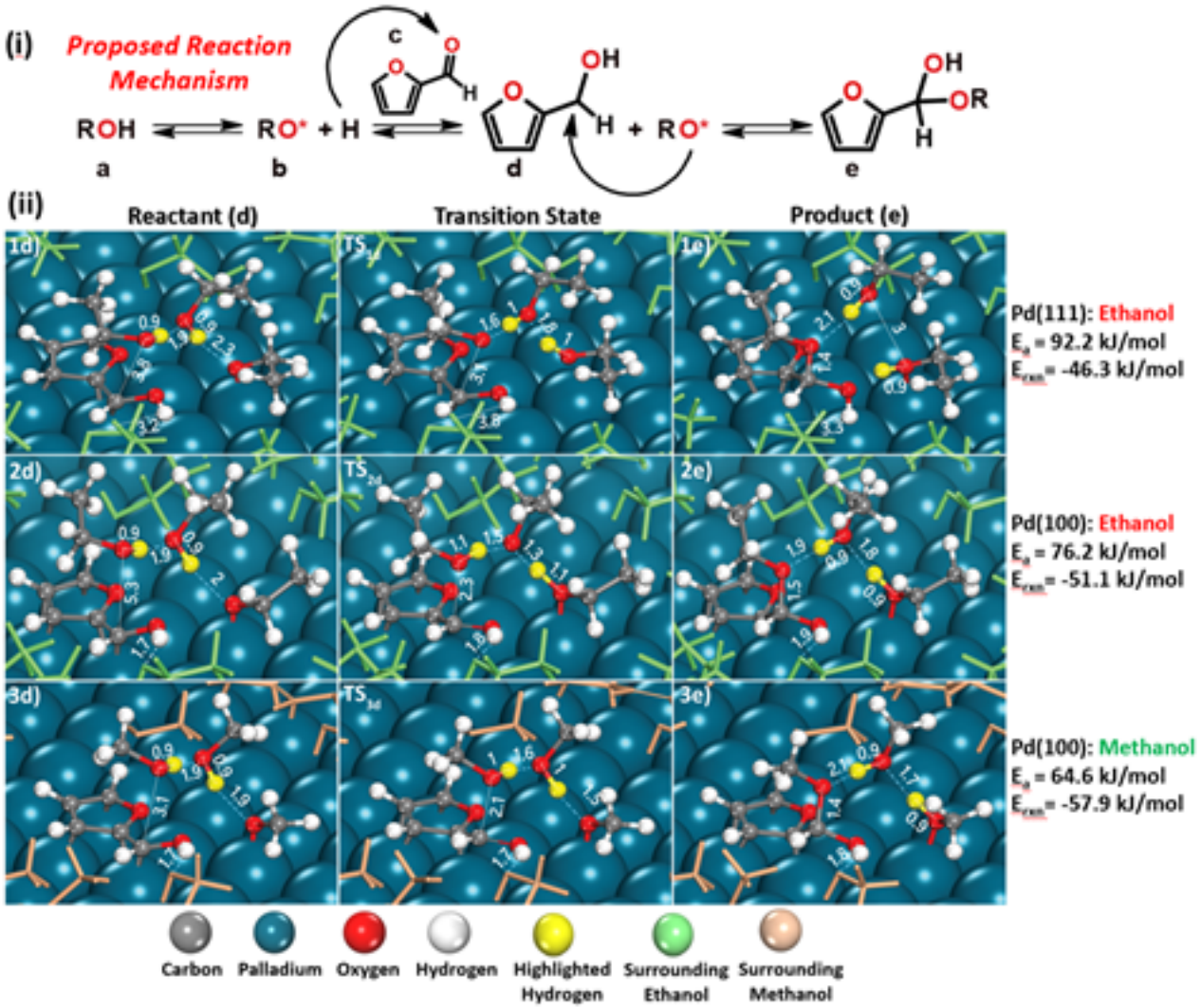

Figure-3: (i) Proposed reaction mechanism for hemi-acetal formation, (ii) Reactant, transition, and product state structures for hemiacetal formation in the presence of explicit ethanol solvent on Pd (111) (1d to 1e), Pd (100) (2d to 2e) and methanol on Pd (100): (3d to 3e). Distances are marked in Å with white dashed lines and hydrogen bonds are shown with blue dashed lines.

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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