ABSTRACT

Humanity is entirely dependent on the finite fossil fuel reserves such as oil, coal and natural gas for energy needs. Due to vast industrialization and explosion in population, the fossil fuel reserves are diminishing at the faster rate which raises concerns over the environment (greenhouse gas and global warming). As no new oil reserves were explored, the number of reserves to production (R/P) ratio decreases, which resulted in the increase in the price of the oil. In addition, the continuous burning of fossil fuel results in the emission of greenhouse gases and the effects are irrevocable. In order to mitigate the twin crises of fossil fuel depletion and environmental degradation, new fuels from bio origin is sought by researchers. As the CO$_2$ recycle time is shorter in biofuels than in burning of fossil fuels, the utilization of energy from renewable biomass offers a promising solution. In addition, utilization of biomass lowers the carbon footprints. Over a last decade, researchers have been focusing on the identification and production of renewable fuels and fine chemicals from various biomasses that includes starch, oils, lignocellulose etc. Among the top value added chemicals reported by U.S Department of Energy, biomass is the most important feed stocks from which various fuels (hydrogen & liquid alkanes) and industrially important building block molecules are obtained. In turn, these platform molecules produce various secondary chemicals and intermediates through energy efficient catalytic processes. Among the various biomasses, lignocellulose is one of the most viable and promising candidate due to its cheap nature, vast availability and it is a carbon- neutral energy resource. Since lignocelluloses are the non-edible portions of plant and do not affect the food chain they are the only alternative to depleting crude reserves.

Lignocellulose can be converted into fuels through biological, thermal and chemical processes. The chemical process gasification of
lignocellulose results in the production of syngas and bio oil. But the hydrolysis is the complex process of deconstructing lignocellulose into various targeted platform molecules which can further be upgraded into fuels through various catalytic processes. The fuels obtained through catalytic processes are of high energy density and have good octane values when compared to ethanol. Since deconstruction of lignocellulose involves many steps, many solid catalysts have been screened for the specific and effective utilization of the biomass into specific products. Among the various catalysts, metal supported catalysts are widely studied in terms of controlled particle size, shape, dispersion, supports and their effect on effective conversion and selectivity towards the desired products.

Supported metal catalysts (mono or bimetallic) are being highly explored for the upgradation of lignocelluloses into fuels and industrially important value added products. Metal supported catalysts are widely used in industrially important processes such as hydrogenation, oxidation, reforming, hydrogenolysis, etc. Among the various support materials, mesoporous support are found to be promising due to their high surface area, tunable pore size, uniform pore volume and stability under harsh reaction conditions. Homogeneous dispersion of the metal nano particles, controlled diffusion of the reactants and products, reduced coke formation and high thermal stability are some of the major advantages of the metal supported mesoporous catalysts. The addition of the second metal acts as a promoter and the method of catalyst preparation improves the activity, selectivity and stability by altering the electronic and geometric properties. Thus the use of bimetallic or multimetallic catalysts offers a new route of producing the desired products with high selectivity and yields.

The present work aims at developing noble metal supported hydroxyapatites for the valorization of biomass derived furfural into value
added chemicals. Hence this study deals with the synthesis of M/HAP, characterization and evaluation of catalytic activity for the conversion of furfural. Literature reveals that Au supported catalysts such as Au/CeO$_2$, Au/ZrO$_2$ and Au/TiO$_2$ catalysts show promising results in the conversion of furfural but studies using monometallic and bimetallic supported over mesoporous hydroxyapatites are scarce. Structurally uniform and porous hydroxyapatite nanorods (HAP) with the gel composition of $1\text{Ca}^{2+}: 0.66\text{PO}_4^{3-}: 0.3$ CTAB: $120\ \text{H}_2\text{O}$ were synthesized under hydrothermal method. The synthesized HAP was impregnated with Au, Pd or Ag so as to obtain either monometallic (Au/HAP, Pd/HAP and Ag/HAP) or bimetallic (Au$_{1-x}$Pd$_x$/HAP and Au$_{1-x}$Ag$_x$/HAP) catalysts. All the hydroxyapatite catalysts were thoroughly characterized by FT-IR, XRD, BET, UV-DRS, XPS, HR-SEM & HR-TEM. Among the bimetals, Au$_{1-x}$Pd$_x$/HAP catalysts exhibit core-shell bimetallic morphology, whereas the Au$_{1-x}$Ag$_x$/HAP catalysts have alloy morphology. The catalytic activities of the bare HAP, monometallic (Au/HAP, Pd/HAP and Ag/HAP) and bimetallic (Au$_{1-x}$Pd$_x$/HAP and Au$_{1-x}$Ag$_x$/HAP) catalysts were evaluated at atmospheric pressure towards the oxidative esterification of furfural to methyl 2-furoate using TBHP as oxidant and methanol as solvent. The current study also focuses on the effect of using various bases (NaOH, NaOCH$_3$ & K$_2$CO$_3$) and oxidants (TBHP, air, O$_2$) on the catalytic activity. Among the various synthesized catalysts, the active/selective Au$_{0.8}$Pd$_{0.2}$/HAP catalyst with core-shell structure showed the maximum conversion of furfural (94.2%) with very high selectivity towards methyl-2-furoate (99%) and the efficiency was maintained even after 5 cycles, supporting the reusability and stability.

Uniform rods of CMK-3 mesoporous carbon materials were successfully synthesized by using nanocasting method. Owing to the hydrophobic nature of the CMK-3, Au nano particles were impregnated into the pores of CMK-3 in acetone by wet impregnation method followed by hydrogen reduction at high temperature (673 K). All the catalysts were thoroughly characterized by various analytical techniques such as XRD, BET,
UV-DRS, XPS, HR-SEM and HR-TEM. Homogeneous dispersion of Au nano particles $\approx 3$nm size was found over CMK-3 materials as evident from HR-TEM analysis. Qualitative and quantitative analyses of Au were made by XPS and ICP techniques. The effect of impregnating metal ions (Ni, Pt and Pd) and supports (SBA-15, graphite, graphene, MWCNT, activated carbon and TiO$_2$) was studied on the catalytic conversion of furfural into methyl 2-furoate through oxidative esterification under methanol medium. Among them, Au/CMK-3 catalyst was found to be the best. Among the Au/CMK-3 catalysts, 5% Au/CMK-3 catalyst showed remarkable conversion of furfural (99.7%) with very high selectivity towards methyl 2-furoate (99.6%). The effect of reaction pressure on the catalytic activity has also been investigated. The stability and reusability of the 5% Au/CMK-3 catalyst was found to be very good even after five catalytic cycles.

Mesoporous Al-SBA-15(25), monometallic (Ru/Al-SBA-15, Sn/Al-SBA-15) and bimetallic (X% Ru-Y% Sn/Al-SBA-15 catalysts (X = 5%, Y= 5%, 10%, 15% and 20%)) were synthesized hydrothermally using P123 as an organic template under highly acidic medium. Metal nano particles were incorporated into SBA-15 via in-situ method and catalytically tested towards the vapour phase hydrogenation of furfural. All the catalysts were thoroughly characterized by XRD, BET, TPD, UV-DRS, HR-SEM, HR-TEM and BET techniques. The hydrogen uptake of the catalysts was recorded using TPR measurements. The fine dispersion of Ru-Sn bimetallics is well identified from the HR-TEM images. Previous reports reveal that wet impregnation method was used for the preparation of catalysts and the reactions were performed through liquid phase hydrogenation of furfural. In the current study, the catalysts were prepared via in-situ method and the hydrogenation of furfural reaction was performed under vapor phase using fixed bed catalytic reactor. The current study also focuses on the effects of varying Ru and Sn contents, reaction temperature, TOS, WHSV, addition of alcohol as hydrogen donors on the conversion and selectivity were studied over the optimized
catalyst (5% Ru-15%Sn/Al-SBA-15). This catalyst was found to be the best as it converts 66% of furfural with the highest selectivity towards the desired products (98%). This catalyst was also found to be stable even after six catalytic cycles.

Structurally uniform mesoporous MCM-41 and Al-MCM-41 were synthesized hydrothermally using CTAB as organic template. 10-50% (w/w) phosphotungstic acid (PTA) was supported over mesoporous Al-MCM-41 by chemical impregnation methods. The synthesized catalysts were characterized by XRD, FT-IR, BET, UV-DRS, Raman, TGA, NH₃-TPD, Pyridine FT-IR, HR-SEM and HR-TEM techniques. The catalytic activities of the synthesized catalysts were tested towards the vapour phase dehydration of glycerol using fixed bed catalytic reactor. The texture properties and acidity of the PTA/Al-MCM-41 catalysts played an important role in the catalytic dehydration of glycerol. The effects of reaction temperature, time on stream, WHSV, glycerol concentration and operating atmosphere on conversion and selectivity were studied and optimized. The highest activity (conversion 92.9% and selectivity towards acrolein 86.3%) was obtained on 40% PTA/Al-MCM-41. In the current study, the optimized catalyst (40%PTA/Al-MCM-41) was prepared by different methods such as vacuum impregnation method (VIM), ultrasonic method (USM), In-situ preparation method (ISM) and Stepwise vacuum impregnation method (SVWM). Based on the results, it was found that the 40% PTA/Al-MCM-41 prepared by ISM method showed the highest catalytic activity (99% conversion and 89.6% selectivity towards acrolein) and was also found to be sturdy for longer times.

The last chapter summarizes the results and general conclusion of the present work. The scope of the future work is discussed at the end.