Chapter VII

Summary and Conclusions
7. **Summary and Conclusions**

This chapter comprises of the summary and conclusions of all the chapters from Chapter I to Chapter VI.

**Chapter I**

Chapter I gives brief introduction about the demand for alternate fuels viz., biodiesel and its advantage and disadvantages. It also explains the synthesis of biodiesel by transesterification reaction using homogeneous and heterogeneous catalysts. The byproduct glycerol formed during biodiesel synthesis is also explained in this chapter and the conversion of glycerol to value added products by transesterification, carbonylation, condensation and acetylation reactions by using solid catalysts is explained in detail based on the literature survey. It gives the gaps found in the literature with respect to this thesis work. The objectives and outline of the thesis are also explained.

**Chapter II**

In chapter II, preparation procedure of all the catalysts taken for the study is explained in detail. Also the catalyst characterization techniques adopted along with the instrument principles are explained in detail in this chapter.

**Chapter III**

This study aimed at designing a novel strong solid base catalyst for transesterification of vegetable oil with methanol. Metal hydroxy stannate was studied for the first time as a catalyst for biodiesel synthesis and catalytic activity was correlated with its physicochemical properties. The CaSn(OH)$_6$ catalyst was thermally stable upto 250 °C with low hygroscopicity exhibiting the morphology of cuboid shape with particle size of 1–2 µm. XRD and FTIR studies confirmed the structure of the catalyst with the presence of OH groups. Estimation of basicity by Hammett Indicator method showed that CaSn(OH)$_6$ has strong basicity. Catalytic activity of CaSn(OH)$_6$ is more efficient than other heterogeneous catalysts in biodiesel synthesis with the biodiesel yield of 94 % for sunflower oil. Further, the application of catalyst was extended to synthesize biodiesel from different non-edible oils as feedstock after the reduction of
acid value from range of 7–14 % to less than 2 %. Catalyst here also proved its capability in synthesizing biodiesel from non-edible oils with yield > 90% in between 9–14 h of reaction time. Physical properties of biodiesel synthesized from various vegetable oils were in the range prescribed by ASTM standards. Moreover, the catalyst showed good activity for 3 cycles of reuse without regeneration at higher temperatures.

Chapter IV

In this chapter, glycerol carbonate is synthesized from glycerol using two different reactants. One is by the transesterification with dimethyl carbonate and other is by carbonylation with urea using solid base and bifunctional catalysts.

Part A

Glycerol carbonate is an important derivative of glycerol which has high potential applications in various fields. It can be used as a raw material for the synthesis of glycidol, polymers, surfactants, lubricating oils as emulsifiers, moisturizers in cosmetic preparations, lustering agents, washing aids and detergents. Glycerol carbonate was synthesized by transesterification of glycerol with dimethyl carbonate using KF supported catalyst. KF was impregnated on various oxides and non-oxide supports like Al₂O₃, SiO₂, ZnO, ZrO₂, H-beta, and carbon to study the influence of the support on the catalytic performance. The preparation procedure of supported KF catalysts was modified to remove weakly adsorbed KF from the catalyst surface. The additional step of water wash of the supported KF catalyst helps in removing the weakly adsorbed KF from the catalyst surface. The generation of basic sites by KF depends upon the extent of KF interaction with the support. Different supported KF catalysts showed an increase in total basicity in the order, KF/carbon < KF/ZrO₂ < KF/SiO₂ < KF/H-beta < KF/ZnO < KF/Al₂O₃. KF/Al₂O₃ catalyst with optimized amount of 3.8 mmol KF, gave the highest activity with 95.8 % glycerol conversion and almost 100 % selectivity for glycerol carbonate. The catalyst showed better performance compared to conventional solid base catalysts such as MgO, CaO and HTc. Among the catalysts studied, KF/Al₂O₃ catalyst was found to be an efficient and
reusable solid base catalyst for the transesterification of glycerol to glycerol carbonate.

**Part B**

Another method of synthesis of glycerol carbonate is from carbonylation of glycerol with urea. Among the raw materials for the synthesis of glycerol carbonate, urea is a cheap and abundant chemical and carbonylation with urea is not well studied reaction. Hence, this reaction becomes more attractive both on scientific and commercial point of view. In this study, zinc hydroxystannate (ZnSn(OH)$_6$) has been reported for the first time as a solid bifunctional catalyst and has been applied for the synthesis of glycerol carbonate from glycerol and urea. Among the different MSn(OH)$_6$ synthesized, ZnSn(OH)$_6$ is proved to be a active bifunctional solid catalyst for the carbonylation of glycerol with urea. Although it is a double metal hydroxide, it possesses low hygroscopicity which makes it a potential catalyst for other base catalyzed organic transformations. It has strong basicity and good thermal stability. The results show that in addition to the strong basicity, Lewis acidic “Zn” in the catalyst act as a promoter for carbonylation reaction of glycerol with urea and facilitate the reaction to get high product yield. It showed excellent glycerol conversion of 98 % with almost 100 % glycerol carbonate selectivity. Leaching test was performed to check the leaching of active species from the catalyst into the reaction medium. The measurement by AAS for Zn content showed the absence of Zn in the reaction mixture. Hence it was confirmed that there was no leaching of active sites during the carbonylation reaction with ZnSn(OH)$_6$. And furthermore, the catalyst also showed good reusability.

**Chapter V**

The condensation of glycerol with acetone to give 5 membered ring compound, solketal (2, 2-dimethyl-4- hydroxymethyl-1, 3-dioxolane) is an important acid catalyzed reaction. Solketal has variety of applications as specialty solvent for gasoline, for cleaning metallic, electrical and plastic substrates and pharmaceutical injections as water miscible solvent. It is also used in cosmetics industry as an additive in ointments, in the chemical industry as an additive in low temperature
transfer fluids. In this chapter, organic-inorganic hybrid catalyst prepared from organic ammonium salt and heteropoly acid was reported for the first time as highly active and selective heterogeneous acid catalyst for the condensation reaction of glycerol with acetone at room temperature. The \((\text{C}_3\text{H}_7)_4\text{N}^+\text{PWA}\) catalyst performed better than other conventional solid acid catalysts like H-beta, amberlyst-15, montmorillonite K-10 and cesium salt of phosphotungstic acid with 94 % glycerol conversion and 98 % selectivity for solketal. And even among all the tetrapropylammonium ions exchanged HPA catalysts, \((\text{C}_3\text{H}_7)_4\text{N}^+\text{PWA}\) gave high glycerol conversion. Different Keggin heteropoly salts (SWA and PMoA) with same alkyl ammonium cation showed similar catalytic activity as that of \((\text{C}_3\text{H}_7)_4\text{N}^+\text{PWA}\). The high activity of \((\text{C}_3\text{H}_7)_4\text{N}^+\text{PWA}\) catalyst can be explained by its acidity and pseudo liquid behaviour. An independent study on the influence of water on catalyst deactivation was performed by adding a small amount of water (glycerol: water (1:1)) during the reaction. The \((\text{C}_3\text{H}_7)_4\text{N}^+\text{PWA}\) catalyst showed a remarkable resistance towards deactivation due to water with only a marginal decrease in conversion (~3 %) compared to other conventional solid acid catalysts like amberlyst-15, H-beta and montmorillonite K-10. \((\text{C}_3\text{H}_7)_4\text{N}^+\text{PWA}\) catalyst was truly heterogeneous and showed good reusability for 3 catalyst recycles.

Chapter VI
In this chapter, glycerol acetins are synthesized from glycerol with different synthetic routes viz. acetylation with acetic anhydride, esterification with acetic acid and transesterification with methyl acetate using different solid acid and base catalysts.

Part A
Glycerol acetylation with acetic anhydride in presence of acid catalyst yields acetins namely monoacetin, diacetin and triacetin (fuel additives). Similarly, esterification of glycerol with acetic acid also forms acetins. Mild reaction conditions were adopted to carry out the reaction using acetic anhydride and acetic acid. Acetylation and esterification of glycerol were studied over various solid acid catalysts namely, amberlyst-15, H-beta, sulfated zirconia and montmorillonite K-10 using acetic anhydride and acetic acid respectively. The performance of the catalyst was measured by glycerol conversion and the selectivity to di and triacetins. The
yields of mono-, di- and tri-acetins were differed with different nature of acid catalysts. The catalysts were characterized by XRD, FTIR, SEM and acidity measurements. The acidity of all the screened catalysts was determined by FTIR-pyridine adsorption, potentiometric acid-base titration using n-butylamine. Among all the catalysts taken in this study, Cs/PWA showed highest activity and selectivity to di and tri acetins. The turn over frequency of all the catalysts increased in the following order; SZ < Amberlyst-15 < H-beta < K-10 < Cs/PWA with highest TOF/h of 267 for Cs/PWA catalyst.

The esterification reactions are predominantly catalyzed by Brönsted acid sites. Thus, the catalytic activity towards esterification of glycerol with acetic acid gives a clear picture with respect to nature of acidic sites (B/L ratio) of catalyst. Cs/PWA with 1.87 and B/L ratio 3.96 showed glycerol conversion of 98 % with high TOF of 30.5 h⁻¹.

Overall, CsPWA exhibited maximum glycerol conversion with higher selectivity towards diacetins and triacetin for both acetylation and esterification reactions (> 98%).

Part B

Transesterification reaction of glycerol with methyl acetate to give di and mono acetins using a solid base catalyst was studied for the first time. Compared to the conventional solid base catalysts used in this study, CaSn(OH)₆ showed high glycerol conversion with high selectivity towards mono and di acetins. The catalysts with higher basicity showed high glycerol conversion with high selectivity towards monoacetin. The selectivity for diacetin was high for metal hydroxyl stannates MSn(OH)₆(M = Mg, Zn, Sr) compared to conventional solid base catalysts except for KF/CaO. High activity and selectivity for diacetin for metal hydroxy stannate in particular, CaSn(OH)₆ could be attributed to the presence of stronger basicity compared with other solid base catalysts.

Chapter VII

This chapter summarizes the conclusions reached in this thesis.