Transition metal based heterogeneous catalysts for valorization of glycerol to glycerol carbonate

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by

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Chapter 7

Summary and Future prospectives

7.1. Summary of the thesis

This thesis is devoted to the catalytic activities of the transition metal based mixed metal oxide catalysts towards the synthesis of glycerol carbonate utilizing bio-waste glycerol as feedstock via transesterification process. In this work Li, Na, Ca and Mg are doped with transition metals and used for designing of heterogeneous catalysts. Different synthesis methods were adopted *viz*., wetness impregnation, coprecipitation method. There has been considerable improvement in conversion and yield of glycerol and GlyC respectively by using the synthesized heterogeneous catalysts. The synthesized catalysts like Li/TiO_2, Na/TiO_2, Ni/CaO, Mg/MnO_2, Mg/CuO were stable and the catalytic activity was almost same up to six runs. The physicochemical properties of the synthesized catalysts support their good activity towards glycerol carbonate synthesis. Green matrix studies were also carried out to ensure the environment compatible nature of the transesterification process. Based on the work carried out, following conclusions is explained.

In **Chapter 1**, the general introduction, literature review and objective of the work is illustrated briefly. An overview of glycerol, a waste product of the biodiesel production process, and biodiesel as an alternative to fossil fuels is provided in Chapter 1. There is a detailed explanation of the discovery of glycerol, its properties, and its importance. The necessity for glycerol value addition and the volume of glycerol produced globally are covered in this chapter. Due to its extensive range of applications in the semiconductor, culinary, pharmaceutical, agricultural, and polymer sectors, glycerol carbonate is one of the main value-added products. Additionally, it covers synthetic technologies with both advantages and disadvantages, the market price and global production of glycerol carbonate, as well as various catalyst types used in reaction processes. The literature on glycerol and its conversion to glycerol carbonate using a variety of heterogeneous and homogeneous catalyst is also summarised in this chapter. This part also discussed the justification for thinking about

heterogeneous catalysts based on transition metal based heterogeneous catalysts for the transesterification of glycerol.

Chapter 2 describes the experimentation methods adopted for the synthesis of the designed catalysts. The physicochemical properties of the catalysts and the activity of the catalyst are studied by performing different characterization techniques. The techniques adopted and formulae used are explained in this chapter. The specifications and purity of the chemicals used in the production of catalysts and the transesterification of glycerol were provided. There was a thorough analysis of the several catalyst synthesis techniques employed in the work, including precipitation, co-precipitation, wet impregnation, etc. The physicochemical characteristics of the catalysts developed were investigated using a number of characterisation techniques, including TGA-DSC, XRD, FT-IR, SEM-EDX, TEM, XPS, and the Hammett indicator method. Additionally, the usage of catalysts in glycerol transesterification is discussed, and the synthetic glycerol carbonate is exposed to ^{1}H, ^{13}C NMR spectroscopy, gas chromatography analysis, and HR-MS spectroscopy in order to measure the glycerol conversion.

In **Chapter 3**, a systematic study of the catalytic activity of the Li modified titanium oxide catalyst towards glycerol carbonate synthesis. We synthesized different weight % of Li loaded TiO_2 catalysts *viz*., 10, 20, 30 named as 10LTO, 20LTO, 30LTO by simple wet impregnation technique, 30LTO calcined at 650 °C was the best catalyst for transesterification of glycerol with DMC. The basic strength and basic sites of Li_2O played an important role in achieving maximum conversion of glycerol to 98.4 % at optimized reaction conditions. TiO_2 had acted as an excellent support and provided significant surface area for the catalytic activity and also acted as Lewis acidic site in mechanism of glycerol transesterification. The overall basic strength and basic sites of the catalysts which influenced yield of GlyC were calculated by Hammett indicator titration method. The activity of catalysts also depended on various

properties of catalyst like crystallinity of catalyst, morphology of catalyst and various reaction parameters like reaction temperature, glycerol to DMC molar ratio, reaction time and catalyst dose, etc.

In **Chapter 4,** Sodium hexatitanate catalyst was prepared by taking different stoichiometric ratios of Na metal (0, 5, 10, 20 wt.%) on TiO_2 calcined at temperature in 400, 700, 900°C range and were tested for transesterification of glycerol. Among all these synthesized sodium titanate catalysts, 10 wt.% Na on TiO_2 (10TNO) calcined at 700° was one of the best catalysts providing highest conversion of glycerol i.e., 98.5 %. The synthesized catalyst was utilized for transesterification of glycerol with DMC and was found to be very efficient. The characterization results demonstrate that the incorporation of Na on titanium oxide lattice enhances the crystallinity forming the pure phase of sodium hexatitanate, i.e., $Na_2Ti_6O_{13}$ which potentially showed its activity towards glycerol carbonate production. In this study, the optimum reaction conditions for transesterification of glycerol were 90 min reaction time, 90°C reaction temperature, DMC to glycerol molar ratio 2:1 and catalyst dose 3 wt.% of glycerol used (in g). The catalyst was active up to fifth cycle in transesterification of glycerol. On the basic of basicity test, it can be concluded that basicity of sodium hexatitanate catalyst plays a major role in the conversion of glycerol-to-glycerol carbonate which shows remarkable performance in transesterification of glycerol. The catalytic activity of prepared $Na_2Ti_6O_{13}$ was evaluated through NMR spectroscopic analysis of the synthesized product and disclosed a good efficiency in mild reaction conditions with 98.5% conversion and 94.5% yield.

In **Chapter 5,** distillation based catalyst has been synthesized by a simple wetness impregnation method via a reaction between raw distillation waste and nickel nitrate at different reaction temperatures. The catalytic efficiency of the synthesized catalyst was investigated for the transesterification of glycerol to GlyC using DMC and glycerol as reactants. The results establish that in contrast to other synthesis methods like coprecipitation

and hydrothermal catalyst synthesis, the wetness impregnation method shows noticeable results for the glycerol conversion. Different reaction parameters were also augmented, and it was found that glycerol to DMC molar ratio, which is 1:3, catalyst amount, which s 300 mg, reaction time 90 mins, and reaction temperature of 90 ℃ are responsible for achieving higher conversion of glycerol of 99.2 % and higher selectivity of 95 % with 94.02 % yield towards glycerol carbonate. Additionally, TOF of the synthesized NDW is 9.74 h^{-1} signifies the good efficiency of the catalyst towards transesterification reaction. To show the environment compatibility of the process followed, green metric parameters are determined, which shows that the synthesis of NDW catalyst and glycerol carbonate follows a greener route. Our results show that distillation waste is an ideal source for making Ni-Ca-O mixed metal oxide catalyst since it decreases the overall cost of the catalyst and, as a result, lowers processing costs. We believe that this information is crucial for developing a highly efficient distillation waste-based heterogeneous catalyst that is cost-effective and environmentally friendly for the manufacture of GlyC on an industrial scale.

In **Chapter 6,** the studies on the effect on support on the activity of catalyst towards glycerol carbonate synthesis has been established. For which, Mg and transition metals like Cu and Mn based catalysts were synthesized by co-precipitation route and applied in transesterification of glycerol. The comparative study of catalytic activity of $MgCu_4O_5$ (CMO) and $MgMn_2O_4$ (MMO) were performed. Among both CMO and MMO catalysts, MMO obtained highest conversion of glycerol i.e., 97 % with 94% GlyC yield whereas CMO provided only 83% glycerol conversion with 71% yield of GlyC. It was observed that the higher basicity of MMO than that of CMO were main reasons behind its higher catalytic activity. The higher oxidation state of Mn i.e. +4 in bifunctional $MgMn_2O_4$ spinel increases the stability of the active basic site (Mg-O) along with increasing the catalytic activity. The suitable optimized reaction parameters for GlyC synthesis using MMO catalyst were 4:1 DMC to glycerol molar ratio,

90°C reaction temperature, 75 min reaction time and 5 wt.% catalyst loading. MMO having strong basic site was highly efficient for GlyC synthesis than that of CMO. The catalyst has high potential and is stable up to sixth cycle. The catalyst has the potential to be applied on industrial scale. This studies establishes the role of support transition metal on the activity of catalyst. Along with providing the stability to the active basic sites, it fastens the reaction by increasing the electrophilicity of the reactant DMC molecules. Therefore, it has been concluded that along with basic metal centre, appropriate choice of acidic metal centre influences the catalytic activity towards the synthesis of glycerol to glycerol carbonate.

The correlation study of the activity of all the synthesized catalyst towards glycerol carbonate production revealed that Ni/CaO catalyst is one of the best catalyst providing appreciable glycerol conversion of 99.2% with 95 % of glycerol carbonate yield. Also, the catalyst is reusable up to six reaction cycles and shows high turnover frequency signifies the potency of the NDW catalyst.

7.2. Future scope of present work

The cost of producing biodiesel can only be decreased by effectively converting crude glycerol into certain products with value-added. In order to address global energy and environmental concerns, the catalytic conversion of renewable biomass resources, such as glycerol, into value-added products, became crucial. For society to flourish sustainably, it is crucial to convert renewable feedstock into value-added chemicals. Glycerol may now be converted into valuable compounds by a number of innovative catalytic conversion techniques that have recently been discovered. Glycerol carbonate is one of the most desirable compounds among numerous value-added products because of its excellent characteristics, including low toxicity, high solubility, good biodegradability, high boiling point, and low flammability. It can be utilised as a solvent in the manufacture of detergents, plastics, resins, and polymers based on glycidol as well as a chemical synthesis intermediate in the manufacturing of polyurethanes, surfactants,

and polycarbonates. When employed as an electrolyte liquid, glycerol carbonate, which has a high flash point and moderate volatility, can be utilised as a lithium-ion battery carrier or additive, a curing agent in cement and concrete, a plant vitalizer stand blowing agent, among other things.

The study uses transition metal based heterogeneous catalysts to synthesize high-quality glycerol carbonate from waste glycerol produced from biodiesel. The extended work of the current study may focus on the use of membrane in lithium-ion batteries and the application of glycerol carbonate in polymer synthesis. Benzo-dioxane, which has numerous uses in the pharmaceutical industry and is also used as an antipyretic drug, can be created by additional chemical interactions between glycerol carbonate and phenol and amine-like chemicals. In addition, glycerol carbonate has potential applications as a green solvent in a variety of chemical industries and as a treatment for kidney ailments. A suitable approach can be developed, and its additional applications can be carried out for future work.