Preface

Starting from powering engines to lighting up the lamps, fossil fuels have become an indispensable part of human life. The use of biofuels like ethanol, butanol and biodiesel as an energy alternative has become a hot topic within the scientific community as it augments in cutting down the greenhouse gas exhausts concurrently providing energy security for the future generations. According to World Bioenergy Association, Europe, United states, Asia are the principal producers of liquid biodiesel. Biodiesel is simple fatty acid methyl esters produced from transesterification reaction of oil, algae or animal derived triglycerides and a monohydric alcohol. However, the production cost of biodiesel is relatively high and leads to co-generation of a major co-product 'glycerol' (10 wt.% of total produce). Glycerol is cheap and highly reactive triol which makes it a potential green platform chemical for the synthesis of board spectrum value added products. Proper utilization of surplus glycerol is a promising transformation as a very small portion of it has direct commercial applications, thence exploration of a smart, sustainable and profitable way of glycerol conversion to value added downstream products like 1,2 or 1,3 diols, dihydroxy acetone, ethylene glycol, mono/di/tri glycerol ethers, hydrogen etc is imperative. Over the recent years, catalytic conversion of glycerol into cyclic carbonate of glycerol i.e. glycerol carbonate (GLC) has increased tremendously due to its unique properties like biodegradability, water solubility, low toxicity and low volatility. These properties of glycerol carbonate are exploited in beauty and personal care industries, as carrier solvents in pharmaceutical industries, surfactants, carrier in lithium ion batteries, component in `membranes for gas separation equipment. Most importantly the presence of both carbonyl and hydroxyl functionalities makes GLC a precursor for synthesis of a variety of polymers including polyesters, polyurethanes and polycarbonates. The conventional synthesis of

glycerol carbonate can be carried out through different pathways depending on the carbonyl source in the feed which may include phosgene, urea, carbon monoxide (CO) and carbon dioxide (CO_2). But these routes have certain major drawbacks like in glycerolysis using urea feed requires continuous removal of ammonia from the reaction system and the formation of isocyanic acid, biuret decreases the rate of GLC formation and makes the process less desirable. In glycerol carboxylation using CO_2 requires high pressure and temperature conditions but provides very low glycerol carbonate yield which greatly increases the production costs. Direct synthesis of glycerol carbonate through transesterification of glycerol and dimethyl carbonate is considered to be the best green pathway as it involves no side reactions, no by-products and the reaction proceeds in equimolar ratios, easy separation of catalyst etc. The transesterification reaction is catalysed by catalyst having appreciable number of active basic sites for the activation of a glycerol molecule. The activated glycerol undergoes nucleophilic addition reaction with activated dimethyl carbonate to give a molecule of glycerol carbonate. Using a suitable catalyst under optimal conditions, for the transesterification process boosts up the yield of desired GLC by chemically activating the reactant species and increasing the reaction rates. Homogeneous bases like potassium (K), sodium (Na) or calcium-based carbonates, alkoxides, hydroxides, and organic ionic liquids (ILs) have already been used for the transesterification process. The major drawbacks of using such homogenous catalysts are the difficult separation procedure after the reaction and leaching out of the catalyst contents during the reaction process. Hence the use of such catalysts is discouraged now- a -days. Lately the use of solid base heterogeneous catalyst has gained much prevalence. Literature showed successful application of mixed metal oxides as effective heterogeneous catalyst for the transesterification process. Mainly both alkali and alkaline earth metal oxides are highly basic in nature and influence the transesterification reaction of glycerol. As a results

investigations were carried out on influence of alkaline earth metal oxides on transesterification reaction of glycerol on the basis of catalyst concentration, reaction temperature, reaction time, glycerol to DMC molar ratios.

This thesis includes synthesis of Mg based heterogeneous catalysts and their application in glycerol carbonate synthesis, physicochemical properties study of designed catalyst, optimization study of entire reaction process, both qualitative and quantitative study of glycerol carbonate and reusability study of catalyst.