Preface

Starting from powering engines to lighting the lamps, fossil fuels have become 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 and Asia are principal producers of liquid biodiesel. Biodiesel is fatty acid methyl esters (FAME) 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 broad spectrum value added products. Proper utilization of surplus glycerol is a promising transformation as a small portion of it has direct commercial applications, hence 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, glycerol carbonate etc. is vital. Over the recent years, catalytic conversion of glycerol into cyclic solketal has increased tremendously due to its unique properties like biodegradability, water solubility, low toxicity, and low volatility. These properties of solketal are used in the beauty and personal care industries, as carrier solvents in the pharmaceutical industries, and as surfactants, disinfectants, and flavoring agents in the food industry. Most importantly, solketal can be described as improving the biofuel properties when blending with gasoline and biodiesel; it enhances the cold flow property, increases the oxidation stability, improves the flashpoint, and reduces gum formation and environmental pollution. Glycerol acetalization is an interesting process that involves the condensation of glycerol with acetone. It 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 acetalization reaction is catalyzed by a catalyst having an appreciable number of active acidic sites for the activation of a glycerol molecule. The activated glycerol undergoes nucleophilic addition reaction with activated acetone to give a molecule of solketal. Using a suitable catalyst under optimal conditions, for the acetalization process boosts up the yield of desired product by chemically activating the reactant species and increasing the reaction rates. Homogeneous acid catalysts like HF, HCl, H_2SO_4, $FeCl_3$, and SnF_2 have already been used for the acetalization process. The major drawbacks of using such homogenous catalysts are the difficult separation procedure after the reaction and the leaching of the catalyst contents during the reaction process. Hence, the use of such catalysts is discouraged. Lately, the use of solid-base heterogeneous catalysts has gained much prevalence. Literature showed the successful application of mixed metal oxides as effective heterogeneous catalysts for acetalization. Metal oxides are used in solketal synthesis, but they show low conversion due to their low acidic nature, and to increase the acidic nature of catalysts, some modifications were performed by the sulfonation process that influences the acetalization reaction of glycerol. As a result, investigations were carried out on the influence of sulfonated metal oxides on the acetalization reaction of glycerol on the basis of catalyst concentration, reaction temperature, reaction time, and glycerol-to-acetone molar ratios.

This thesis includes a study on the synthesis of sulfonated transition metal-based heterogeneous acid catalysts and their application in the synthesis of solketal, a physicochemical properties study of the designed catalyst, an optimization study of the entire reaction process, and both a qualitative and quantitative study of solketal, and a reusability study of the catalyst.