Catalytic conversion of bio-glycerol to glycerol carbonate using Mg based heterogeneous catalysts

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by

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CHAPTER 7

Overall conclusions & work summary

This thesis provides an overview of Mg based mixed metal oxide catalysts and their application in glycerol carbonate synthesis from bio-waste glycerol. In this work Mg with other metals were used for designing of catalysts via several processes. There has been considerable improvement in conversion and yield of glycerol and GLC respectively by using the synthesized Mg based heterogeneous catalysts. All the synthesized catalysts like Mg/ZnO, NiMgOx and $MgCr_2O_4$ were stable and the catalytic activity was almost same up to six runs. Based on the work carried out, following conclusions have been drawn.

7.1 Synthesis of glycerol carbonate by using Mg/ZnO catalyst

i. Among different weight percentage of Mg doped ZnO catalysts (1,3,5,7...) synthesized by simple wet impregnation technique, 3wt.% Mg/ZnO catalyst calcined at 550°C was the best catalyst for transesterification of glycerol with DMC.

ii. The basic strength and basic sites of MgO enhanced maximum conversion of glycerol to 98.4 % at optimized reaction conditions.

iii. ZnO 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.

iv. The overall basic strength and basic sites of the catalysts which influenced yield of GLC were calculated by Hammett indicator titration method.

v. The activity of catalysts also depended on various properties of catalyst like surface area, crystallinity of catalyst, morphology of catalyst and various reaction parameters like reaction temperature, glycerol to DMC molar ratio, reaction time and catalyst dose, etc.

7.2 Synthesis of glycerol carbonate by using NiMgOx catalyst

i. NiMgOx catalysts were prepared by taking different molar ratios of Ni and Mg metal (1:1, 1:2, 1:3 …) calcined at temperature in 500 to 800°C range and were tested for transesterification of glycerol.

ii. Among all these synthesized nickel magnesia catalysts, 3:1 MgNi calcined at 700° was one of the best catalysts providing highest conversion of glycerol i.e., 97 % with 80.04% GLC yield.

iii. Catalyst with 3:1 MgNi molar ratio has the maximum basic strength and highest basicity and it had shown very good activity in GLC synthesis.

iv. The study of effect of calcination temperatures (between 500 to 800°C) revealed that 3:1 MgNi 700° has the maximum activity which ascribed to the presence of good surface area and presence of high density of strong basic sites.

v. 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 4:1 and catalyst dose 4wt% of glycerol used (in g).

vi. The catalyst was active up to sixth cycle in transesterification of glycerol providing 90% conversion.

7.3 Synthesis of glycerol carbonate by using MCO and MVO spinel like catalysts

i. Mg and transition metals like Cr and V based spinels were synthesized by co-precipitation route and applied in transesterification of glycerol.

ii. The comparative study of catalytic activity of $MgCr_2O_4$ (MCO) and MgV_2O_4 (MVO) were performed.

iii. Among both MCO and MVO catalysts, MCO obtained highest conversion of glycerol i.e., 99.2 % with 95.7% GLC yield where as MVO provided only 83% glycerol conversion with 76.45% yield of GLC.

iv. The higher surface area and higher basicity of MCO than that of MVO were main reasons behind higher conversion percentage of glycerol in case of MCO catalyst.

v. The suitable optimized reaction parameters for GLC synthesis using MCO catalyst were 4:1 DMC to glycerol molar ratio, 85°C reaction temperature, 80 min reaction time and 5wt% catalyst loading.

vi. MCO having high surface area ~ $28.7 m^2/g$ and strong basic site was highly efficient for GLC synthesis than that of MVO possessing relatively lesser surface area of about $23.8 m^2/g$.

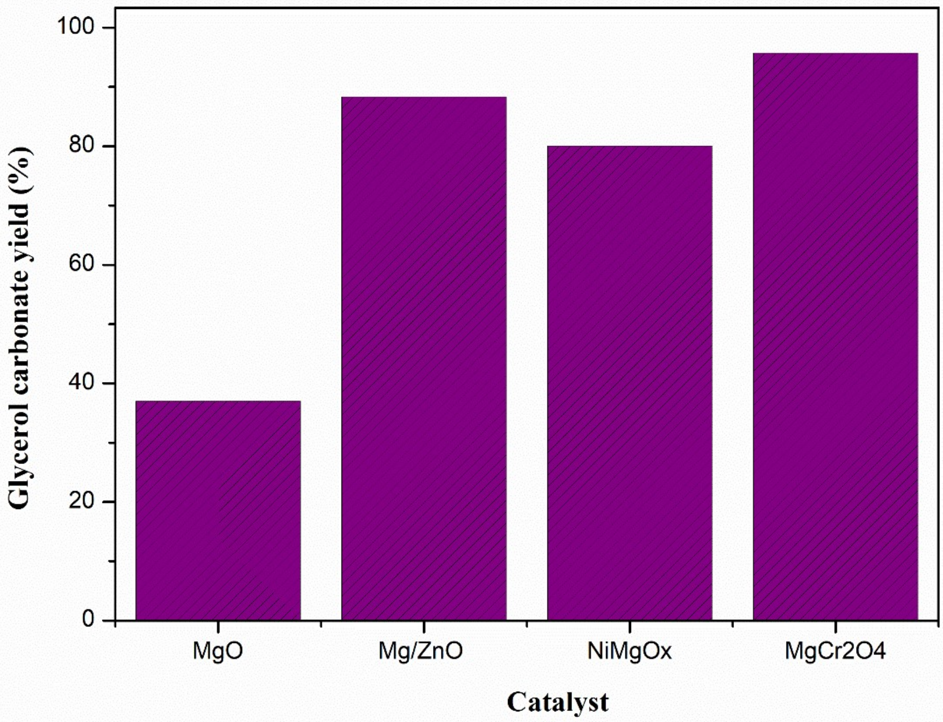

Fig 7.1 Correlation of activity of catalyst with glycerol carbonate yield (%)

A comparison of conversion of glycerol by using pure MgO and Mg with other metal mixed oxide catalyst has been given in fig 7.1 and it is revealed that MCO is one of the best catalysts providing highest conversion of glycerol (99.2%) than other catalysts used in this work. The catalyst has high potential and is stable up to sixth cycle.

7.4 Future scope of present work

Current study presents synthesis of high-quality glycerol carbonate from bio waste glycerol derived from biodiesel using Mg based heterogeneous catalysts. The extended work of present study could be directed towards application of glycerol carbonate in polymer synthesis and use of membrane in lithium-ion batteries. Glycerol carbonate could further undergo chemical reactions with phenol and amine like compounds to form benzo-dioxane which has broad applications in pharmaceutical industries and also acts as antipyretic medicine. Apart from this, glycerol carbonate could be used as a green solvent in many chemical industries and also help in curing renal diseases. An appropriate methodology can be devised and its further applications can be executed for future work.

Synopsis

The thesis entitled "**Catalytic conversion of bio- glycerol to glycerol carbonate using Mg based heterogeneous catalysts**" mainly based on the study of glycerol carbonate synthesis from waste bio-glycerol derived from biodiesel using magnesium based heterogeneous catalysts like Mg doped zinc oxide (Mg/ZnO), Nickel magnesia catalyst (NiMgOx) and Magnesium chromate ($MgCr_2O_4$).

Prior to the discovery of fossil fuels, human society mainly depended on plant biomass to meet the energy demand worldwide. The discovery of crude oil in 19th century created an inexpensive liquid fuel source which helped to industrialize the world. Now- a-days petroleum oil and diesel have become the longstanding primary energy sources. The emerging economic, political and environmental factors forced mankind to look for alternative fuels or to develop energy efficient and cost-effective processes for the sustainable production of fuels and chemicals. Biofuels generate significantly less greenhouse gas emissions than the fossil fuels. Among biofuels, biodiesel has been receiving great attention for the past few decades due to its renewable and eco-friendly nature. Biodiesel has been produced in a large scale worldwide during the past few years, and its production is expected to increase in the coming years too. The development and commercial use of biodiesel has been rapidly expanding in many European as well as in Asian countries. Despite the rapid pace of biodiesel development and commercialization, there are several key challenges emerging and these must be addressed efficiently. One key fact is that during biodiesel production, approximately 10 wt.% of glycerol is produced as bi-product and remains as a glut in the market. The crude glycerol is a major drawback in biodiesel industries and hampers the market competitiveness of biodiesel, as a result, in order to economize the biodiesel production, the valorisation of glycerol to several value-added products is the main focus of researcher now- a-days. Glycerol has broad platform in foods, cosmetics, pharmaceuticals, explosive, triacetin, tobacco industries, however, the markets are saturated and cannot absorb large amount of glycerol coming from the increasing production of biodiesel. During the past decade intense research activity has been initiated worldwide to find new profitable uses for glycerol which could reduce both environmental pollution and economic issues. The usage of low quality of glycerol derived from biodiesel industries is a big challenge as this glycerol cannot be used for direct food and cosmetic applications. Hence, the price of glycerol will continue to drop commensurate with supplies of glycerol coming into the market from the biodiesel industry. Alternatively, the effective conversion of crude glycerol to specific value-added products will reduce the biodiesel production cost. The catalytic conversion of renewable biomass resources like glycerol to value added products became important to reduce the worldwide energy and environmental issues. The conversion of renewable feedstock into value added chemicals is an essential step for the sustainable development of society. Recently, a series of novel catalytic conversion processes that transform glycerol into useful chemicals have been reported. Among various value-added products, glycerol carbonate is one of the most valuable chemicals because of its ideal properties like low toxicity, high solubility, good biodegradability, high boiling point and low in flammability. It can be used in as a solvent in cosmetics, medicine, an intermediate in organic synthesis, synthesis of poly carbonates, surfactants, polyurethanes and production of detergents, plastics, resins and glycidol based polymers. Glycerol carbonate having high flash point and low volatility is used as electrolyte liquid carrier or an additive in lithium-ion batteries, a curing agent in cement and concrete, plant vitalizer stand blowing agent etc. However,the synthesis of glycerol carbonate can be carried out through different pathways depending on the carbonyl source in the feed which may include phosgene, urea, CO, CO_2. But these routes have certain drawbacks like in glycerolysis using urea feed requires continuous removal of ammonia from the reaction system as well as the formation of undesirable side products like isocyanic acid and biuret which decreases the rate of glycerol carbonate yield. The carboxylation of glycerol using CO_2 requires high pressure and temperature conditions but gives a low glycerol carbonate yield which greatly increases the production costs. The synthesis of glycerol carbonate through transesterification process is regarded as one of the best green pathways as it involves no side reactions, no by-products, the reaction proceeds in equimolar ratios and easy separation of catalyst and solvents are achieved. 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 DMC to give a molecule of glycerol carbonate. Using a suitable catalyst under optimal conditions, the transesterification process boosts up the yield of the desired GLC by chemically activating the reactant species and increasing the reaction rates. Cyclization occurs in the intermediate resulting in the formation of glycerol carbonate. Strong bases like potassium, sodium or calcium-based hydroxides, alkoxides, carbonates and organic ionic liquids 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 content during the reaction process. Hence, the use of such catalysts is discouraged and lately the application of solid base heterogeneous catalyst in glycerol valorisation has gained prevalence. Whilst heterogeneous catalyst has conquered all the demerits and is recyclable too, it has gained attention. Incorporation of dimethyl carbonate further enhances the greener approach of the transesterification reaction and also tailors the reaction pathway as methanol is the only side product formed in this process. However, the transesterification reaction needs to be catalysed by a suitable catalyst in mild conditions for effective conversion of glycerol. Literature suggests that there was enormous study of both alkali and alkaline metal-based catalysts like Li/ZnO, Ca/La, KNO_3/MgO, $NaAl_2O_3$, $BaCO_3/C$, Ca/ZrO_2 etc in glycerol carbonate synthesis. But there are very few studies of Magnesium-based catalysts on the synthesis of glycerol carbonate, although it exhibits very good basic properties and high surface area. As Magnesium (Mg) is cheaper, nontoxic, easily available in many forms, possessing reliable basic strength and basic site which is one of the important criteria for transesterification of glycerol, our research work is focussed towards the broad study of Magnesium based heterogeneous catalysts and their application in valorisation of bio-glycerol to glycerol carbonate.

The current thesis contains seven chapters.

Chapter 1. Chapter 1 gives a brief introduction of biodiesel as alternative to fossil fuels as well as glycerol produced as waste during biodiesel production process. The discovery, physical properties and importance of glycerol are well explained. The global production of glycerol and why the value addition of glycerol is required are discussed in this chapter. Glycerol having multifunctional properties extended its applications towards various reaction processes like esterification, dehydration, oxidation, etherification, acetalization, halogenation, glycerolysis, polymerisation, etc. Among several value-added products like lactic acid, 1,3-PDO, 1,3 -DHA, solketals, hydrogen, polyesters, and glycerol carbonate; glycerol carbonate is one of the important value-added products due to its broad applications in semiconductor industries, medicines and food industries, agriculture, and polymer industries. The market value and worldwide production of glycerol carbonate, synthetic methods with both advantages and disadvantages, and types of catalysts used in reaction processes are briefly discussed in this Chapter 1.

Chapter 2. This chapter includes literature survey of glycerol and its valorisation to glycerol carbonate using various types of heterogeneous and homogeneous catalysts. The types of reaction processes involved in glycerol carbonate synthesis, such as direct carbonylation, glycerolysis using urea and transesterification reaction and types of catalysts: homogeneous or heterogeneous, ionic liquids, enzymes used and their suitability for reaction process were reported. The reaction mechanism involved in transesterification of glycerol-to-glycerol carbonate was also thoroughly explained in this chapter. Here, we also discussed the reason behind for consideration of magnesium based heterogeneous catalysts for transesterification of glycerol.

Chapter 3. This chapter incorporates the materials and methods adopted for the present research work. The chemicals used in designing of catalysts and transesterification of glycerol were mentioned with specification and purity. The synthesis for catalyst adopted in the work like precipitation, co-precipitation, wet impregnation, etc. were broadly discussed. The physicochemical properties of synthesized catalysts were studied by several characterization techniques like TGA-DSC, XRD, FT-IR, SEM-EDX, XPS, BET-surface area and Hammett indicator method. It also covers the application part of catalysts in transesterification of glycerol and the synthesized glycerol carbonate undergoes ^{1}H and ^{13}C NMR spectroscopy, gas chromatography analysis for obtaining conversion percentage of glycerol.

Chapter 4. This chapter introduces a new Mg based heterogeneous catalyst and its application in glycerol carbonate synthesis. The Mg doped ZnO catalyst was synthesized by simple wet impregnation method and the properties of catalyst were studied by various techniques like TGA-DSC, XRD, FT-IR, XPS, SEM-EDX, BET-surface area and Hammett indicator titration method. The synthesized catalyst was applied for glycerol carbonate synthesis via transesterification. The conversion of glycerol was found to be 98.4 ± 0.5% with 88.34 ± 0.5 % yield of glycerol carbonate under optimized condition of reaction parameters like DMC: glycerol molar ratio 4:1, temperature 80°C, time 120 min and 3wt% catalyst loading with respect to glycerol used in grams. As the main beauty of heterogeneous catalysts are their reusability so the study of reusability of catalyst was performed and it was noted that the catalyst was stable up to sixth runs providing 91% conversion of glycerol. The conversion percentage of glycerol was calculated using proton NMR spectra and also through gas chromatography.

Chapter 5. Chapter 5 included the synthesis and application of bimetallic nickel magnesia ($NiMgO_x$) catalyst in transesterification of glycerol. Varying the molar ratios of Mg keeping Ni content constant (1:1NiMg,1:2 NiMg,1:3 Ni Mg …...), the catalysts were synthesized via co-precipitation route. The synthesized catalysts were tested for transesterification of glycerol and the catalyst which provided highest conversion of glycerol was selected for further studies. Similarly, the physicochemical properties of designed catalysts were investigated by sophisticated techniques viz. TGA-DSC, XRD, XPS, SEM-EDX, etc. The maximum conversion percentage of glycerol using 3:1 Mg Ni catalyst was found to be 97±0.5 % at optimum reaction conditions, such as temperature 90°C, time 90 min, DMC to glycerol molar ratio 4:1 and 4 wt. % of catalyst loading. The nickel magnesia catalyst was regenerated and recycled up to six runs providing 88.34±0.5% conversion of glycerol. The reason behind deactivation of catalyst was also studied by leaching test. The synthesized products were confirmed by gas chromatography and NMR spectra.

Chapter 6. This chapter illustrates the comparative study of two Mg based spinel catalysts namely $MgCr_2O_4$ and MgV_2O_4 for synthesis of glycerol carbonate. Both the spinels are synthesized by co-precipitation route and were used for transesterification of glycerol. The physicochemical properties of MCO and MVO catalysts were investigated and compared by TGA, XRD, XPS, SEM-EDX, BET-surface area, etc. Both the catalysts were tested for transesterification of glycerol via reflux condensation process. The conversion and yield (%) of glycerol and glycerol carbonate at optimized reaction conditions were compared. Among both the catalysts, MCO opted higher percentage of conversion of glycerol than that of MVO catalyst. The reason behind higher catalytic activity of MCO than that of MVO was studied and proved. Under optimized reaction conditions, MCO provided 99.2±0.5 conversion of glycerol along with 95.7± 0.5 % yield of glycerol carbonate whereas MVO provided 76±0.5 % conversion of glycerol. The lower surface area and lower basicity of MVO are mainly responsible for poor conversion percentage of glycerol. Catalyst reusability study suggested that MCO possessed appreciable catalysing potential and stability for six runs giving 86 ± 0.5 % conversion.

Chapter 7. This chapter includes the overall summary of the work carried out and recommendations for glycerol carbonate synthesis process.

All the data obtained from experimental work has been summarized in Table 7.1. The table shows that Mg based heterogeneous catalysts (Mg/ZnO, NiMgOx, $MgCr_2O_4$) synthesis techniques and optimized conditions for transesterification of glycerol. On the basis of outcome of this thesis, it can be concluded that Mg based heterogeneous catalysts have been found to be highly effective for transesterification reaction of glycerol. It has been observed that waste bio-glycerol provides appreciable percentage of glycerol carbonate yield. Hence, it is concluded that glycerol derived from biodiesel plants has industrial importance for large scale production of glycerol carbonate.

Table 7.1 Summary of the experimental work

Chapter	**Mg based catalysts**	**Catalyst synthesis process**	**Optimization condition**	**Glycerol conversion (%)**	**GLC yield (%)**	**Reusability of catalyst**
4	Mg/ZnO	Wet impregnation	3wt% of catalyst, 4:1 DMC to glycerol molar ratio, 80°C temperature, 120 min time	98.4 ± 0.2	88.34±0.32	6 times
5	NiMgOx	Co-precipitation	4wt% of catalyst, 4:1 DMC to glycerol molar ratio, 90°C temperature, 90 min time	97± 0.3	80.04±0.5	6 times
6	$MgCr_2O_4$	Co-precipitation	5wt% of catalyst, 4:1 DMC to glycerol molar ratio, 85°C	99.2±0.13	95.7±0.26	6 times

			temperature, 80 min time			