CHAPTER 2

Literature Review

2.1 Introduction

This chapter deals with the study of many literatures on glycerol carbonate synthesis from waste glycerol using heterogeneous catalysts. In many literatures particular emphasis has been given to characterization of catalysts and the co relationship between the catalysts and their catalytic activity in glycerol transesterification reaction.

2.2 Glycerol production and consumption

During transesterification reaction of edible and non-edible oils glycerol is produced as a by-product. Around 10 wt.% of glycerol is produced as a waste during biodiesel production process. Europe is one of the largest producers and consumer of biodiesel which shares 90% of global biodiesel production. U.S and Brazil are now ramping up for production at a faster rate than Europe and expected to excel in near future. It is estimated that biodiesel could replace more than 30% of all on - road diesel used in Brazil, Europe, India and U.S. by the year 2025 [83]. Being cleaner, renewable and greener by nature, biodiesel has been proved to be a valuable fuel for Petro-diesel engine. In addition to this United States replaced 2% of the on-road diesel with biodiesel in a B2 policy by 2012 and almost 363 million kg of new glycerol was added to the market. The global glycerol market size is expected to reach USD 3.5 billion by 2027, expanding at a CAGR of 4.0 [84]. Improved standard of living coupled with growing consumer demand for high quality and innovative personal care products is expected to drive the market over the forecast period. Asia pacific is one of the prominent consumers as well as exporter of glycerol with major exporting countries being Indonesia and Malaysia. Abundant raw material availability and high biodiesel production is further contributing to the glycerol production in the region. Various countries like Russia, Germany, Netherlands, and Denmark are contributing to the largest imports in the region. Glycerol is identified as an important building block for future biorefineries by Department of Energy, (DOE) USA [85] . Economic forecasts have demonstrated that the net production cost of B100 type biodiesel can be reduced from US$0.63 per litre to US$ 0.35 per litre by adding value to the glycerol by-product [86-87].

2.3 Catalytic conversion of glycerol to value added products.

Glycerol having three hydroxyl groups has broad platform for the production of several value-added products not only due to surplus amount but also due to its very good characteristics like non-toxicity, bio sustainability and bio-degradability. From a technical standpoint, glycerol's multifunctional structure and properties can be tailored by several different reaction pathways. Furthermore, the conversion of glycerol to various value-added compounds contributes to the use of clean renewable energy sources. In this aspect catalysis represents a critical approach to green chemical technology in the activation and utilization of glycerol. It is revealed that both homogeneous and heterogenous catalysts have been used for the transformation of glycerol to value added products. As a results a series of novel catalytic approaches have been used through different reactions for conversion of glycerol [88–90].

2.4 Catalytic approach in glycerolysis reaction

Glycerol carbonate being one of the value-added products of glycerol has gained attention over the last 20 years due to its versatile reactivity and industrial application in lithium-ion batteries and in other applications. Several synthetic pathways for glycerol carbonate are widely used by application of catalysts. The glycerolysis reaction of glycerol with urea also catalysed by both homogeneous and heterogeneous catalysts. Various catalysts like $MgSO_4$, $ZnSO_4$, zinc containing solid catalysts like ZnO, smectite, hydrotalcite, $ZnCl_2$, $ZnSO_4$, $Zn(CH_3COO)_2$ etc were used for efficient conversion of glycerol to glycerol carbonate[91- 93]. The application of $ZnCl_2$ and $ZnSO_4$ provided 84% and 81% conversion of glycerol with 97 % and 92% selectivity towards glycerol carbonate respectively. Hydrotalcite exhibited appreciable conversion of 82% with 80% selectivity of glycerol carbonate [94-95]. Fujita et al.,2012 [35] obtained GLC from glycerol and urea using Ga, Zn, and Au supported on ZSM-5 zeolite. The order of carbonylation activity of all these catalysts are Au > Ga > Zn. [35]. Manjunathan et al.,2016 [92] reported complex of Zn as catalyst for synthesis of glycerol carbonate from glycerol and urea. They obtained 98% conversion of glycerol with 83% GLC yield. In this reaction process isocyanate was formed as an intermediate along with metal mono-glycerolate which further rearranged to form GLC.

Similarly, Sajidah et al.,2016 [93] reported that 2.5%Au /MgO provided 81% conversion of glycerol with 68% GLC selectivity in glycerolysis reaction of glycerol with urea and the catalyst was active up to ten cycles. Zuhaimi et al., 2015 [96] reported glycerolysis of urea using γ- Zirconium phosphate as catalyst and obtained 80% conversion of glycerol with 100% selectivity towards GLC under mild reaction condition. Perin et al.,2020 [97] reported 0.5wt% La_2O_3 as an acid catalyst for glycerolysis reaction of urea and obtained 91% GLC yield at temperature 140°C for 1h reaction period. The Lewis acidic nature of catalyst highly influenced the conversion of glycerol-to-glycerol carbonate to a certain extent. Zhang et al.,2018 [98] synthesized GLC using calcined Ce-NiO at 150°C with pressure of 4.0×10^{-3} mPa and found 61% yield of GLC after 2h. Similarly, Aresta et al., 2006 [99] obtained 69% yield of GLC using Co_3O_4 /ZnO catalyst at optimum reaction condition of temperature 145°C, 4h time and 0.1 mPa pressure. From the catalytic activity results it can be noticed that strong basic oxides like Mg/Al hydrotalcite exhibited 97% yield of GLC at 130°C, 0.1 mPa for 1h reaction time, which was reported by Alvarez et al., 2010 [23]. During glycerolysis reaction with urea in presence of catalyst it is noticed that the Lewis acid activates the carbonyl group of urea and conjugate base activates the hydroxyl group of glycerol which facilitates the reaction process and provided very good conversion of glycerol.

2.5 Catalytic approach in carbonylation of glycerol

Several research groups have been investigating the direct synthesis of glycerol carbonate by reaction of glycerol with carbon monoxide or carbon dioxide. In this synthetic route mainly two types of catalytic systems were reported to provide good yields of GLC such as Cu (I) catalysts and $PdCl_2$ with KI. Tin (Sn) based catalysts were first reported for carbonation of glycerol with CO_2.In these direct synthetic routes alcoholic solvents like methanol , ethanol are added to accelerate the reaction rate and improve the yield percentage of GLC[96]. Many other catalysts like rhodium complexes with phosphine ligands, MgO, organic bases (1,5,7-triazabicyclo [4,4,0] de-5-ene), ceria-based catalyst, Sn catalysts under supercritical CO_2 conditions have been used for glycerol carbonate synthesis. George et al., 2009 [100] proposed synthesis of glycerol carbonate from glycerol via CO_2 addition in presence of catalyst n- $Bu_2Sn(OMe)_2$ and obtained only 7% of yield at high temperature 180°C for 15h reaction period using 5mPa pressure. Again they obtained 35% yield of glycerol carbonate using n-Bu_2SnO catalyst at optimized condition of 80°C, 5mPa pressure, in 4h reaction time using methanol as a solvent during the reaction process[100] . It is suggested that glycerol carbonate could be synthesized through the reaction of glycerol with carbon monoxide and oxygen in presence of catalysts and additional solvent. Similarly, Hu et al., 2010 [101] proposed another catalyst like $PdCl_2$(phenanthroline) with KI for synthesis of glycerol carbonate in solvent medium DMF. They obtained 85% of GLC yield at optimized condition of temperature 140°C, 3mPa pressure, and 2h of reaction time [101]. Thermodynamic calculations showed that the reaction of glycerol with CO and CO_2 are thermodynamically limited. Since carbonation of glycerol suffers from high pressure requirement, thermodynamic limitations, use of toxic solvents, very expensive catalyst systems and low GLC yield, which dramatically increases the production costs, as a result a much safer and greener alternative for GLC synthesis is the main focus of the researchers.

2.6 Catalytic approach in transesterification of glycerol

Transesterification reaction being one of the versatile and simple method for glycerol carbonate synthesis, many catalytic systems have been reported in literature for synthesis of GLC from glycerol with DMC till date. The main advantages of transesterification process are it require very simple reaction set up, green process and from economic point of view it is very flexible for both industry and lab as well. This reaction process is also catalysed by both homogeneous and heterogeneous catalysts. Rokicki et al., 2005 [102] reported Mg-Al hydrotalcite catalyst for glycerol carbonate synthesis via transesterification of glycerol with DMC and obtained 82% of GLC yield at optimised reaction condition of 100°C for 1h reaction time. They used the layer anionic clay, hydrotalcite, in which the anionic species such as carbonate and hydroxide were located in between the layer due to charge compensation of positively charged brucite layer. Song et al., 2017 [103] reported Li/ZnO catalyst for synthesis of glycerol carbonate and obtained 96% conversion of glycerol at optimized reaction condition of temperature 85°C, for 90 minutes of time. Although the catalyst was efficient in conversion of glycerol but the stability of catalyst was only up to 4th times run in reaction process. The deactivation of catalysts was mainly due to leaching of metal ions after a certain extent i.e., four times run in transesterification reaction. Galadima et al., 2017[104] prepared ionic liquids immobilized on mesoporous MCM-41and tested the performance of the catalyst in the synthesis of GLC. High temperature and longer reaction time were favourable for the catalyst reactivity. The catalyst was reused for three consecutive runs without any loss of its initial activity. Wang et al., 2018 [71] proposed Mg/Al/Zr catalysts for transesterification of glycerol with DMC and obtained very good conversion of glycerol 99% with in 1h at 90°C of reaction temperature. Similarly, Simanjuntak et al., 2013 [74] reported Mg/La catalyst for glycerol carbonate synthesis and obtained 94% yield of GLC at mild reaction condition of 75°C and 90 min reaction time. They also well explained the mechanistic pathways for the formation of GLC. The above catalyst was highly stable and recyclable up to six times providing significant conversion of glycerol. Marakatti et al., 2015 [105] reported metal ion exchanged zeolites as highly active solid acid catalyst for the synthesis of GLC by transesterification reaction of glycerol with DMC. They also proposed a mathematical model of reactor to obtain the kinetic parameters at suitable optimized reaction conditions. In this experiment mass balances were built into the reactor model and order of the reaction was fixed. The chemical equilibrium for GLC synthesis was calculated and theoretical calculation was compared with experimental data and matched. The authors concluded that transesterification of glycerol with DMC was thermodynamically favourable for GLC production according to equilibrium constant. Temperature has also important role in this reaction process increasing temperature can increase the chemical equilibrium constant and vice versa. Literatures suggested the deactivation of alkali and alkaline based solid catalysts for transesterification of glycerol like CaO, $Ca(OH)_2$, KOH, Ca $(OCH_3)_2$ etc. The conversion of glycerol was decreased dramatically when the catalysts were recycled because of the conversion of all the basic catalysts in to their corresponding carbonates after the first run in reaction process [104-105] . There were dissolution losses of the catalysts in the reaction medium. Bai et al.,2011 [79] reported KF modified hydroxyapatite as a very efficient heterogenous catalyst for synthesis of glycerol carbonate using DMC with glycerol. This catalyst provided 93% yield of GLC with 99% conversion of glycerol at optimised reaction condition of temperature 78°C for 50 min. it was easily recovered and recycled catalyst and the catalytic activity was highly comparable with homogeneous KF catalysts. Similarly, another catalyst namely NaOH/γ -Al_2O_3 was reported by Bai et al., 2013 [106] for glycerol carbonate synthesis. This catalyst was also proved to be one of the efficient heterogeneous catalysts for transesterification of glycerol. Authors found that under the condition of 2:1 DMC to glycerol molar ratio, at 78°C, for 1h reaction time the conversion of glycerol reached up to 97.9% along with 99% selectivity of GLC. The comparative study of catalytic activity of NaOH/γ -Al_2O_3 with other catalysts specially with K_2CO_3 showed that former catalyst was much better than latter one with respect to its conversion percentage of glycerol and basicity also[106] . Trimethyl amine (TEA) being one of the homogeneous catalysts was used in transesterification of glycerol with DMC reported by Ochoa-Gomez et al., 2012 [107]. They studied the conversion of glycerol optimizing the reaction parameters like temperature, DMC to glycerol molar ratio, time etc and found that at 68°C, 4:1 DMC to glycerol molar ratio and after 2.5h, at 90°C the GLC yield reached up to 98%. They also proposed a reaction mechanism to justify the product yield using such homogeneous catalyst. Although it provided very good conversion of glycerol but the separation of catalyst for further use in same reaction process was too difficult. Basic ionic liquids were also utilized for synthesis of glycerol carbonate by many researchers, for instance Naik et al.,2009 [108] reported quaternary ammonium salt for synthesis of GLC and obtained very good yield of 93%. In this process pure product was isolated in quantitative yield using a threefold excess of DMC and 15% of ionic liquids. Here they obtained that the IL could be reused at least four times without any significant reduction in the conversion and yield. Similarly, Sandesh et al., 2013 [109] approached transesterification of glycerol with DMC using KF supported catalyst. Here several oxides and non-oxide supports like SiO_2, Al_2O_3, ZnO, ZrO_2 etc were used to enhance the support on catalytic activity. They modified the method of synthesis of supported KF catalysts in order to remove weakly adsorbed KF from the catalyst surface. The generation of basic sites mainly depends upon the extent of interaction of KF with support material. Among many supported KF catalyst KF/Al_2O_3 showed highest activity with 95.8% conversion of glycerol and 100% selectivity of GLC. The catalyst had zero leaching of metal atoms as compared to other supported KF catalyst and exhibited better catalytic performance with 5th time recyclability [109]. Liu et al., 2013 [110] proposed a series of hydrotalcite like layered double hydroxides (LDH) with different atomic ratios of Mg/Al by co-precipitation route. They reported the effect of calcination temperature on the activity of Mg/Al catalyst and found variable conversion percentage of glycerol. In this work they noticed that the calcination temperature highly influenced the basicity of catalyst and enhanced the rate of transesterification reaction of glycerol. They also investigated the co relationship between surface basic density of catalyst and the catalytic activity and found that the activity of LDH catalyst was directly proportional to surface density of basic sites[110]. Finally, they concluded that LDH calcined at 600°C exhibited maximum conversion of glycerol i.e., 96% at optimised reaction condition. Similarly, Khayoon and Hameed., 2013[111] reported a highly effective catalyst namely $Mg_{1+x}Ca_{1-x}O_2$ calcined at 850°C for transesterification of glycerol. The best reaction condition for providing highest conversion of glycerol about 98% with 100%GLC selectivity was 1:2 glycerol to DMC molar ratio, 70°C for 90 min reaction time under atmospheric pressure. The synergism interaction between Ca and Mg species in the catalyst structure was highly responsible for efficient production of glycerol carbonate. Hervert et al.,2014 [112] reported N-heterocyclic carbenes as efficient organo-catalysts for GLC synthesis from glycerol and DMC. They got very good yield of GLC for a reaction time of 30 min at room temperature. Various amin based catalysts were tested for synthesis of GLC by Qing et al., 2018 [113] from glycerol using DMC. In this work amidines like 1,8-diazabicyclo [5,4,0] undec-7-ene (DBU) and 1,5- diazabicyclo [4,3,0] non-5-ene (DBN) were found to be very suitable catalysts for this reaction. The obtained 98% conversion of glycerol with 96% selectivity of GLC with DBU as catalyst [113-114]. Wang et al., 2019 [115] proposed a catalyst from waste baby diaper (DBDWS-500) for transesterification reaction of glycerol with DMC. They got 95.6% conversion of glycerol with 93.6% GLC yield at optimised reaction condition of 4:1 DMC to glycerol molar ratio, for 60 min at 75°C. The catalyst was highly stable up to 8th cycle providing 92% conversion of glycerol. Similarly, another waste material derived catalyst like RK-30% - 800 was synthesized by Mohanty et al., 2019[116] and applied in transesterification of glycerol. In this work they studied the doping of various alkali and alkaline earth metals (K, Sr and Mg) on to red mud with different weight percentages and also with different calcination temperature. They concluded that K-doped red mud catalysts were found to have better activity as well as stability than other Sr and Mg doped catalysts for transesterification reaction of glycerol. The better activity of RK-30%-800 catalyst was mainly due to presence of maximum surface concentration of active K_2O which significantly contributed to increase the basic properties of catalyst than other metal doped RM catalyst. They got 98% conversion of glycerol with 94% GLC yield at optimised condition of 90 min reaction time at 75°C under normal atmospheric pressure and 3:1 DMC to glycerol molar ratio.

There are few reports related to application of Mg based heterogeneous catalysts in transesterification of glycerol with DMC till date, although it belongs to alkaline earth metal category having very good basic properties. As magnesia is widely studied material due to its very high thermal stability, biological and chemical activeness, high surface area, high thermal conductivity and low electrical conductivity and high solubility in water, acid and ammonia. Magnesia having high surface area, nanocrystalline structure, redox properties and basic character acts as catalysts in many reactions process like dry reforming, oxidative dehydrogenation, dehydrohalogenation, water gas shift reaction and transesterification reaction. In this work, we explored the catalytic activity of Mg based heterogenous catalysts for synthesis of glycerol carbonate and reported various properties of catalyst responsible for effective activity towards GLC. The main focus of our work was to synthesize Mg based catalysts and their application in GLC synthesis via transesterification of glycerol with DMC.

2.7 Reaction Mechanism involved in transesterification reaction of glycerol

A plausible reaction pathway for synthesis of GLC was proposed using glycerol and DMC by the concept of conventional transesterification process where both acidic and basic sites of catalysts take part in reaction. It can be observed that the reaction pathway follows cyclic mechanism with four steps shown in fig 2.1. According to the mechanism, the basic sites of catalyst react with glycerol to abstract H^+ ion from primary hydroxyl group of glycerol and form glyceroxide anion ($C_3H_7O_3^-$). In second step that anion reacts with DMC to produce an adduct and a methoxide anion. In the third step glyceroxide anion reacts with DMC to form hydroxyl alkyl carbonate intermediate which is very highly unstable by nature. In the fourth step that intermediate undergoes cyclisation to form glycerol carbonate and methanol as side product. After the formation of GLC the catalyst was free and again used for synthesis of GLC. Since the catalyst was further used for GLC synthesis and follows that cyclic path as a result the overall mechanism is known as cyclic reaction mechanism. The overall mechanism suggested that a base catalyst is essential to increase the conversion of glycerol, more is the basic strength higher will be the catalytic activity [111,115-117].

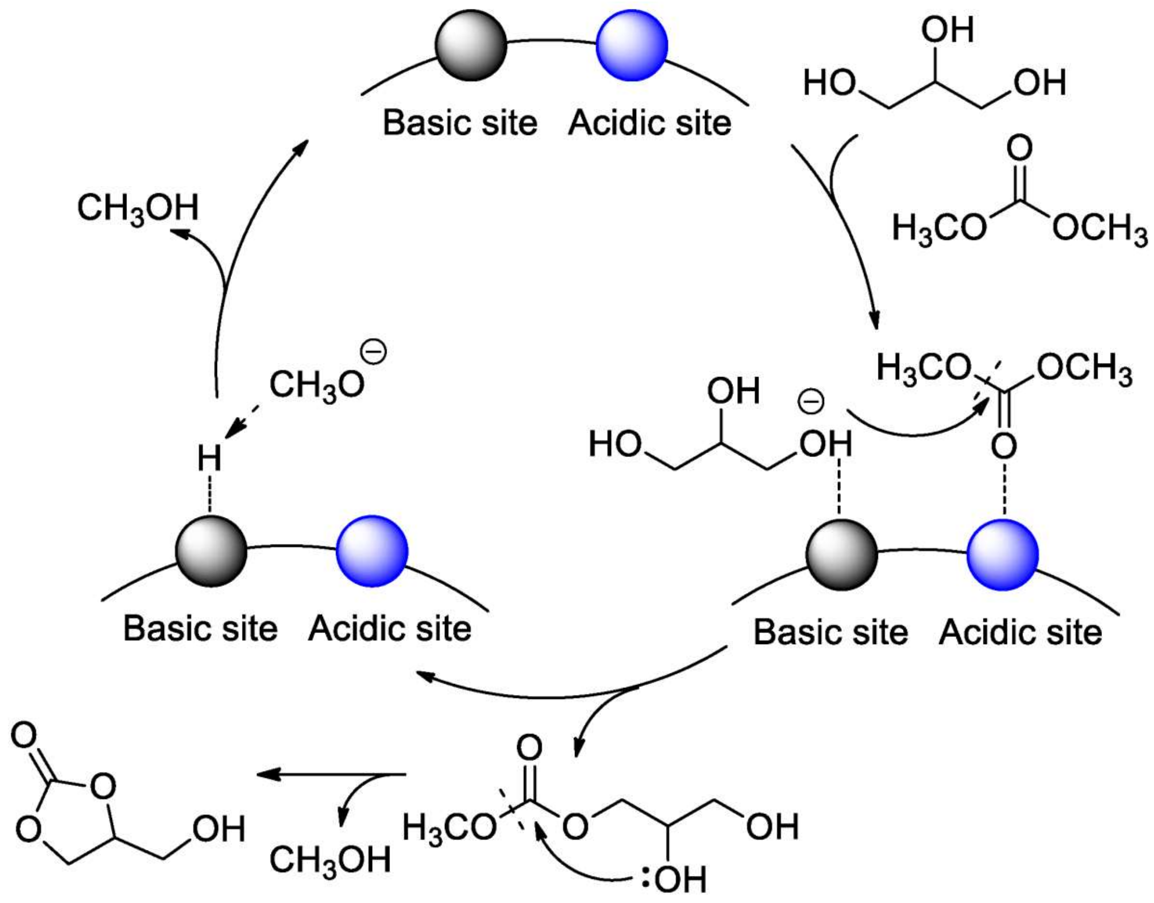

Fig 2.1 Plausible reaction mechanism for glycerol carbonate synthesis from glycerol and DMC.