CHAPTER 4

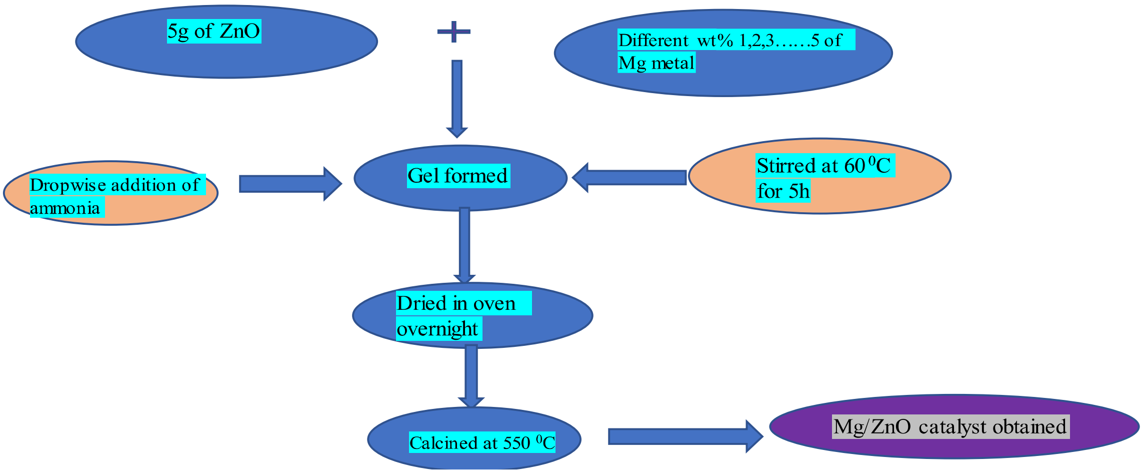
Synthesis of glycerol carbonate using Mg doped ZnO heterogeneous base catalyst

4.1 Introduction

This chapter includes the synthesis of Mg doped ZnO catalyst as a heterogenous catalyst by simple wet impregnation method and its application in glycerol carbonate synthesis. Here different wt.% of Mg like 1,3,5,7 and 10 wt.% were doped to ZnO and calcined at various temperatures ranging from 150° to 750°C and tested for conversion of glycerol. The physico-chemical properties of synthesized catalysts were analysed by various techniques like X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), Brunauer-Emmett-Teller (BET) surface area analysis, Barrett-Joyner-Halenda(BJH) analysis and basicity study by Hammett indicator titration method. The synthesized glycerol carbonate was also analysed by gas chromatography (GC) and both ^{1}H and ^{13}C NMR spectra. The main objective of this work was to develop a catalyst which is cost effective and suitable for complete conversion of glycerol with lower temperature and short duration through transesterification process. It was noticed that the MgO had strong basic sites and high surface area in alkaline earth metal atoms. It has greater possibilities to improve the catalytic activity with less consumption of time and temperature during trans-esterification reaction. Hence, the synthesis and application of Mg based ZnO catalyst was investigated.

4.2 Synthesis of Mg modified ZnO catalyst (Mg/ZnO)

Mg doped ZnO catalysts utilized in glycerol transesterification reaction were prepared by wet impregnation method. In a typical preparation process, 5 g of ZnO was impregnated using 50 mL of $Mg(NO_3)_2$ aqueous solution of appropriate concentration. The resulting mixture was then stirred at ambient temperature for 6h with addition of ammonia solution to maintain pH 9-10. After certain time gel type solution was formed which was dried at 100°C for 10 h and then calcined at an appropriate temperature for 5 h to get the corresponding catalyst. The obtained catalyst was named as nMg/ZnO-T, where n and T represented Mg loading and calcination temperature, respectively. For example, 5 wt.% Mg supported on ZnO calcined at 350°C was denoted as 0.05Mg/ZnO-350. Similarly, Mg/ZrO_2, Ba/ZnO, Sr/ZnO, K/ZnO were prepared by simple wet impregnation method and calcined at 550^{0}C for 5h as like Mg/ZnO as mentioned above. All the prepared catalysts were utilized for glycerol carbonate synthesis.



Scheme 4.1 Synthetic method of Mg/ZnO catalyst by simple wet impregnation technique.

4.3 Characterization of Mg/ZnO catalyst

4.3.1 TGA-DSC study

The thermal behaviour of uncalcined 3wt%Mg/ZnO catalyst was studied by TGA-DSC analysis and represented in figure 4.1. It was observed that the weight loss of the un-calcined catalyst occurred in two steps. The initial weight loss of the compound started within 120-450°C and it might be due to removal of surface and residual water from the sample. The second weight loss of the sample had occurred in the range of 450-600°Cdue to decomposition of nitrate ion in order to form stable metal oxides. Above 550°C, there was no noticeable weight loss shown in TGA curve, since the formed metal oxide became stable in that temperature range and the thermo gravimetric curve became parallel as well. From the figure, it was also observed that the endothermic peak around 300°C may be due to desorption of water, which assigned to phase transition of catalyst.

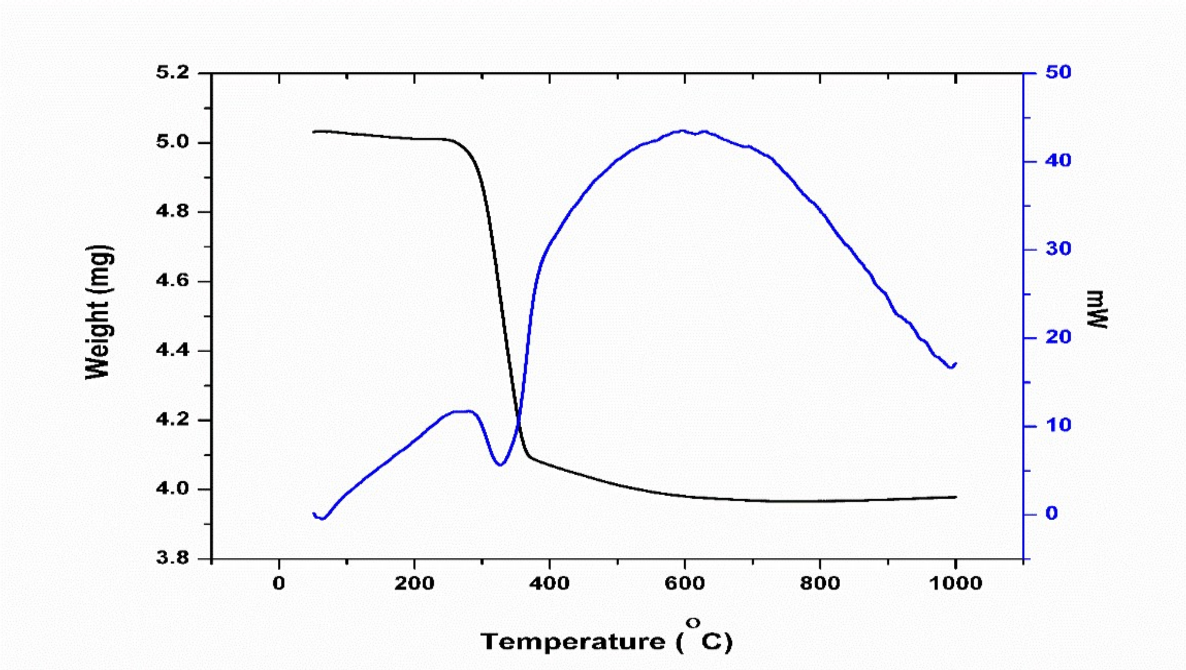


Fig 4. 1 TGA-DSC curve of synthesized 3 wt % Mg/ZnO catalyst

4.3.2 X-ray diffraction pattern (XRD)

The X-ray diffraction patterns of ZnO and Mg doped zinc oxide with various weight percentage and calcined at 550^0C is shown in fig 4. 2(a). All the diffracted peaks were matched with JCPDS file -891397 and cleared that all the samples are crystalline with hexagonal cubic crystal structure. It is clear from the XRD pattern that there is no reflected peak of magnesium nitrate or magnesium oxide which might be due to either higher doping of Mg ions or dispersion of magnesium nitrate on the surface of zinc oxide. As it is known that the atomic number of an atom affects the scattering factor of the atom, the weak diffractions of lighter atoms are undetectable in presence of heavier atoms like zinc as a result the diffracted peaks of magnesium were absent which accounted for the high scattering factor of Zn^{2+} upon Mg^{2+}[118].

The Mg^{2+} ions doped into ZnO lattice was explored and shown in fig 4.2(b) with in 2θ range 34-38^0.The diffracted peaks having miller indices values (002) and (101) were shifted to lower diffraction angles with increasing Mg^{2+} content as compared to pure ZnO which assigned to the replacement of Zn^{2+} (74pm) by Mg^{2+} (78pm) in crystal lattice of ZnO as a result there was creation of asymmetry in crystal structure. Depending on these results, we concluded that there was substitution of partial Zn atom with entering of Mg atoms in ZnO crystal up to a certain concentration, above that there was aggregation of Mg^{2+} ions on ZnO grains as a secondary phase [119–121] .

Fig 4.2(c) depicts the X-ray diffraction pattern of 3 wt% Mg/ZnO calcined at different temperatures. Although there was no change of diffraction peaks after treatment with various calcination temperatures but the peaks were highly intensified with rise of temperature which might be due to growth of ZnO crystal at high temperature. To get the broad idea related to the effect of calcinations temperature, the diffraction peaks within 2 θ range 34-38^0 were studied and presented in fig 4.2(d). The peak at 36.46^0 with miller indices (101) Mg doped ZnO shifted to lower diffraction angle as compared to pure ZnO minimized to 36.38^0 at 350^{0}C and then shifted to higher diffraction angle 36.49^0 at 550^{0}C and lastly returned back to 36.37^0 at 750^{0}C which might be due to alteration of ZnO with Mg^{2+}. At very low temperature the substitution of Zn^{2+} in ZnO lattice did not occur as Mg^{2+} was very inactive at this temperature and the interaction between Zn^{2+} and Mg^{2+} lead to formation of intermediate state which lengthened the Zn – O bond and caused asymmetry in ZnO lattice which accounted for lower diffraction angle. At 550^{0}C the diffraction peaks returned back to original position with ZnO due to very identical ionic radii between Zn^{2+}

and Mg^{2+} and the diffracted peak having miller indices (101) moved to lower diffraction angle after 750^{0}C which might be due to creation of single phase of ternary $Mg_{2x}Zn_{1-x}O$ [122].

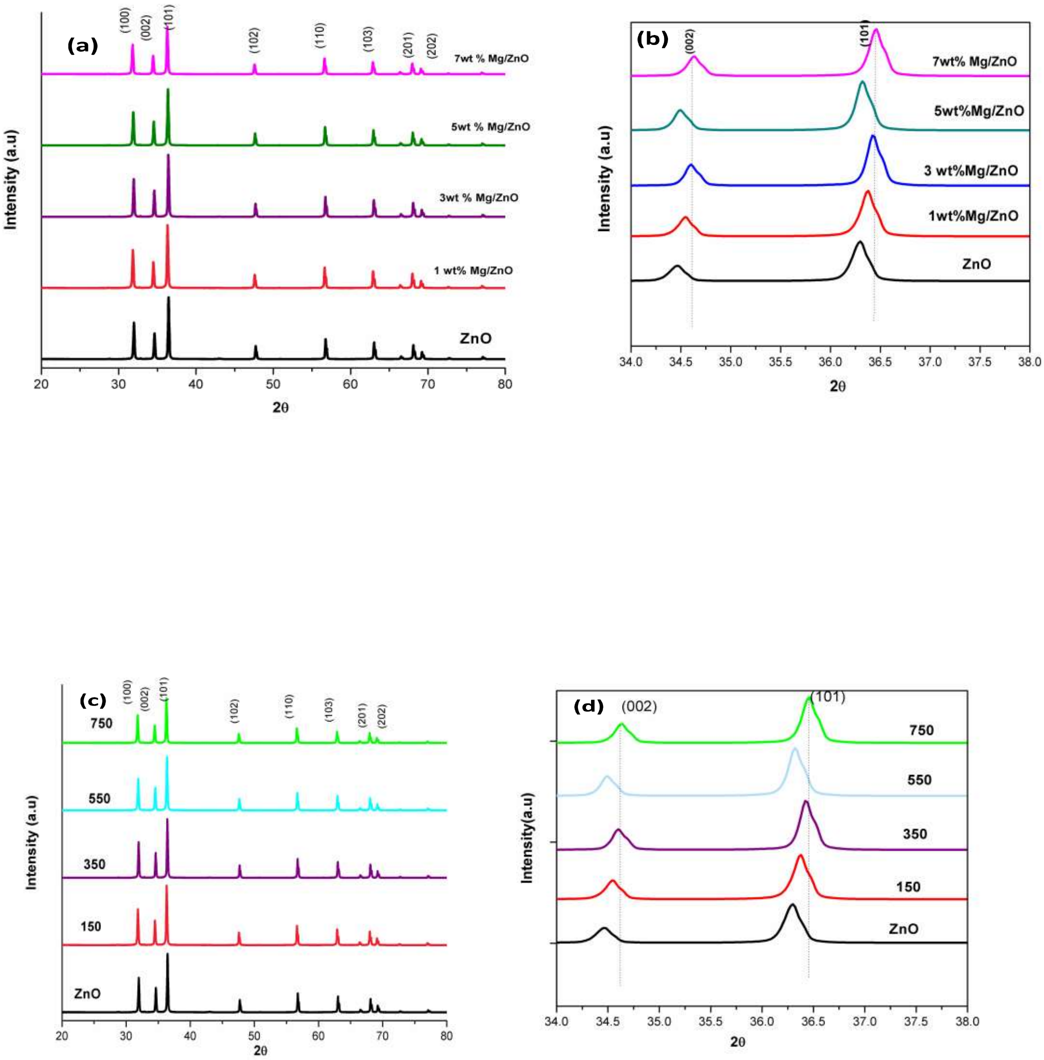


Fig 4.2 XRD pattern of (a) ZnO and ZnO with different wt.% of Mg loading calcined at 550^{0}C, (b) with in 2θ range 34-38^0 (c) 3 wt.% Mg/ZnO calcined at different temperature. (d) 2θ = 34-38^{0}Ccalcined at different temperature.

4.3.3 FT-IR spectra

The functional groups present in synthesized Mg/ZnO catalysts were well explored through FT-IR spectroscopy and depicted in figure 4. 3. The vibration bands in the range of 400-600 cm^{-1} are intense and broad in all samples which might be due to zinc metal and oxygen sub-lattice vibration. The peak around 1382 cm^{-1}can be considered due to the carbonate ion (CO_3^{2-}) in the commercial ZnO. Another band at 1652 cm^{-1} is due to bending vibration of O-H bond of water molecule also highly intensified with increasing loading percentage of magnesium nitrate, while the appearance of broad absorption band at 3478cm^{-1} may be due to the O-H stretching vibration of surface H_2O [123–125] .

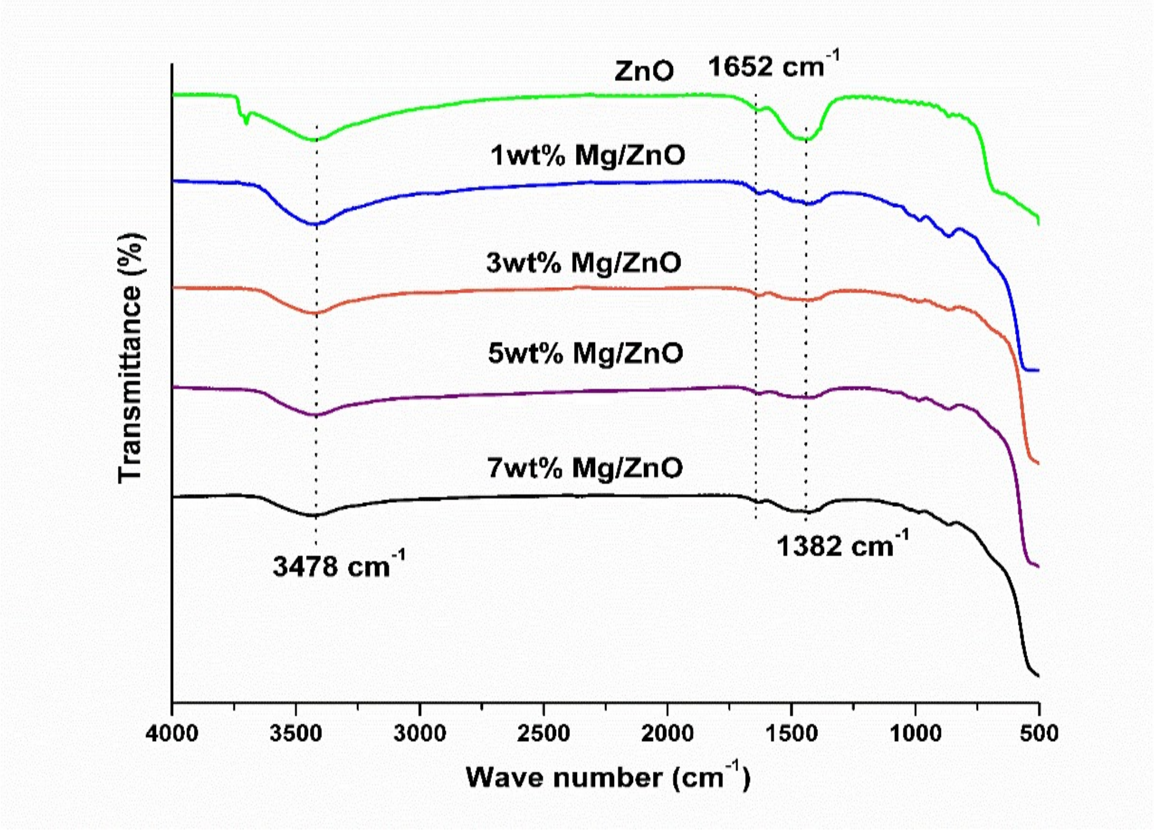


Fig 4. 3 FT-IR spectra of synthesized Mg/ZnO catalyst calcined at 550°C

4.3.4 SEM -EDX study

The SEM image of Mg doped ZnO were presented in fig 4.4 . It was observed that morphology of the catalyst was uniform having variable grain sizes. The average particle size of 1wt% Mg/ZnO and 3wt% Mg/ZnO at 550°C are 248 and 293 nm respectively signifying that the particle size is purely dependent on loading amount of magnesium content as the loading amount of magnesium content rises the particle size increases. The increase of calcination temperature of the catalyst can also be considered for the larger particle size of the catalyst like as for 3wt% Mg/ZnO 550^0C the particle size 1.64μm increased to 1.75μm when calcinations temperature increased to 750^0C for the same catalyst which indirectly matches with the XRD result as there is formation of new phase along with larger crystals being formed at higher calcinations temperature. There was no significant change of particle size of 3wt%Mg/ZnO after five times run, fig 4.4 (c) indicating the morphology of the catalyst is stable after five runs in transesterification reaction of glycerol. The compositional analysis through EDS anticipated that the magnesium, zinc and oxygen are the elements exist in the sample and shown in fig 4.5. The existence of all the elements in the oxides forms can be confirmed due to presence of high amount of oxygen and also the presence of Mg in bimetallic mixed oxide with zinc enhances the basicity, heterogeneity and stability of the catalyst [126].

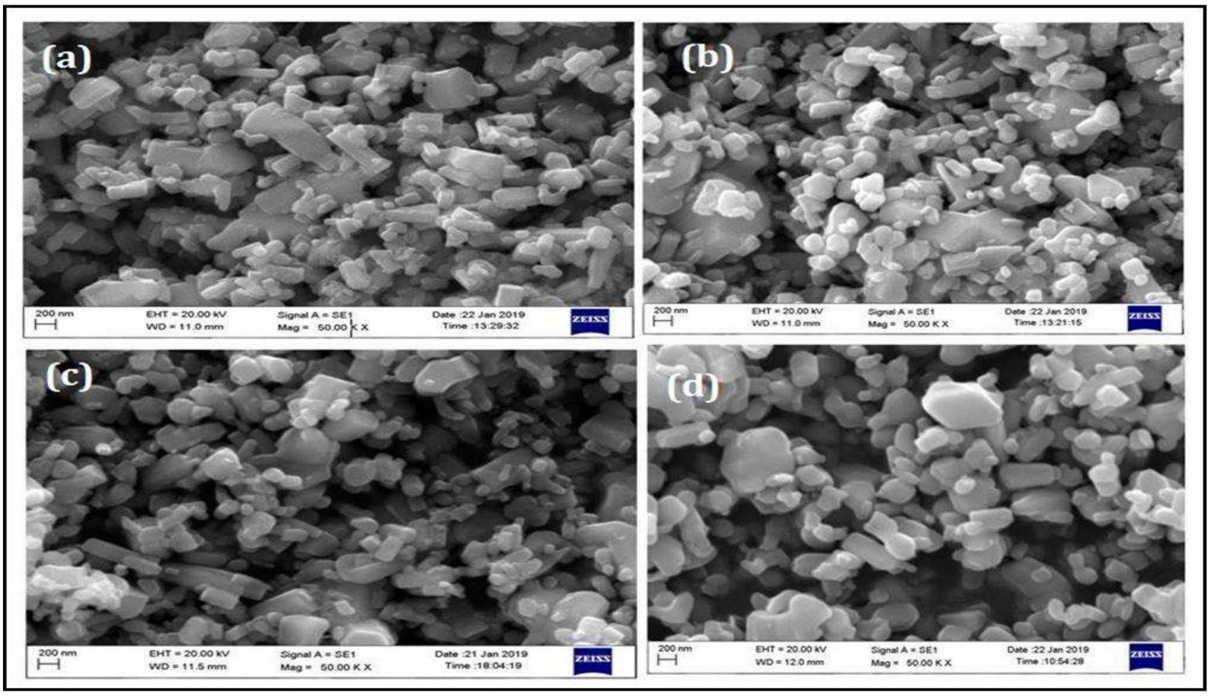
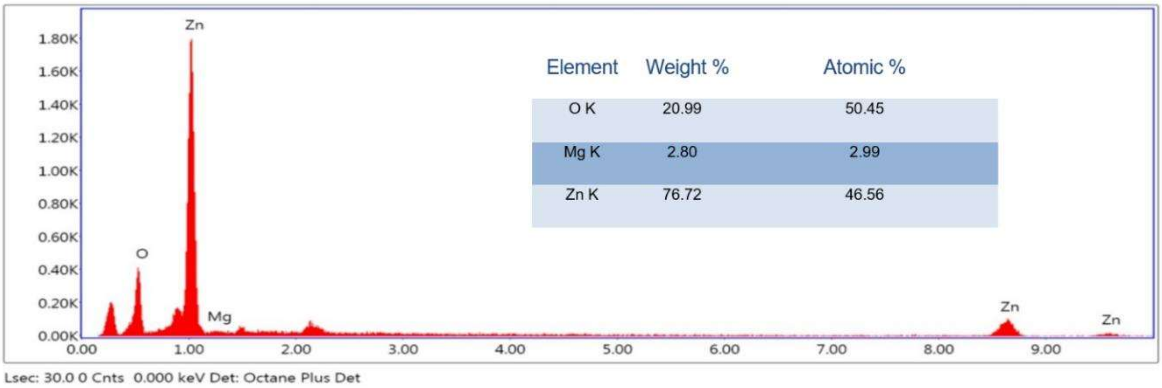


Fig 4.4 SEM micrograph of synthesized catalyst (a) 1 wt % Mg/ZnO-550^{0}C; (b) 3 wt % Mg/ZnO- 550^{0}C; (c) 3 wt % Mg/ZnO reused (d) 3 wt %Mg/ZnO 750°C



Element	Weight %	Atomic %
O K	20.99	50.45
Mg K	2.80	2.99
Zn K	76.72	46.56

Fig 4.5 EDX profile and Element composition of 3wt%Mg/ZnO catalyst calcined at 550^{0}C.

4.3.5 XPS study

The XPS analysis of 3wt% Mg/ZnO was carried out and the obtained graph was represented in fig 4.6. The peaks of different elements were calibrated with carbon 1s peak centred at 284.6 eV. The two different peaks at binding energy 1021.5eV and 1044.7eV correspond to Zn $2p_{3/2}$ and $2p_{1/2}$ of ZnO respectively indicating that the Zn is at +2 oxidation state and it is in agreement with XRD analysis. For Mg, the peak is observed at 1304.2 eV and it can be assigned to 1s of MgO. The deconvolution of the peak of O1s spectra was observed and it was resulted into two peaks at the binding energy of 529.6eV and 530.8eV respectively. The peak at 529.6eV can be considered due to O 1s spectra for the oxide of Zn and Mg due to lattice O^{2-}. Moreover, the peak at 530.8eV can be assigned for bridging oxygen between both metals[126,127]. These results are in agreement with the NIST XPS database and their oxidation states are also in agreement with the crystalline phase obtained from XRD analysis.

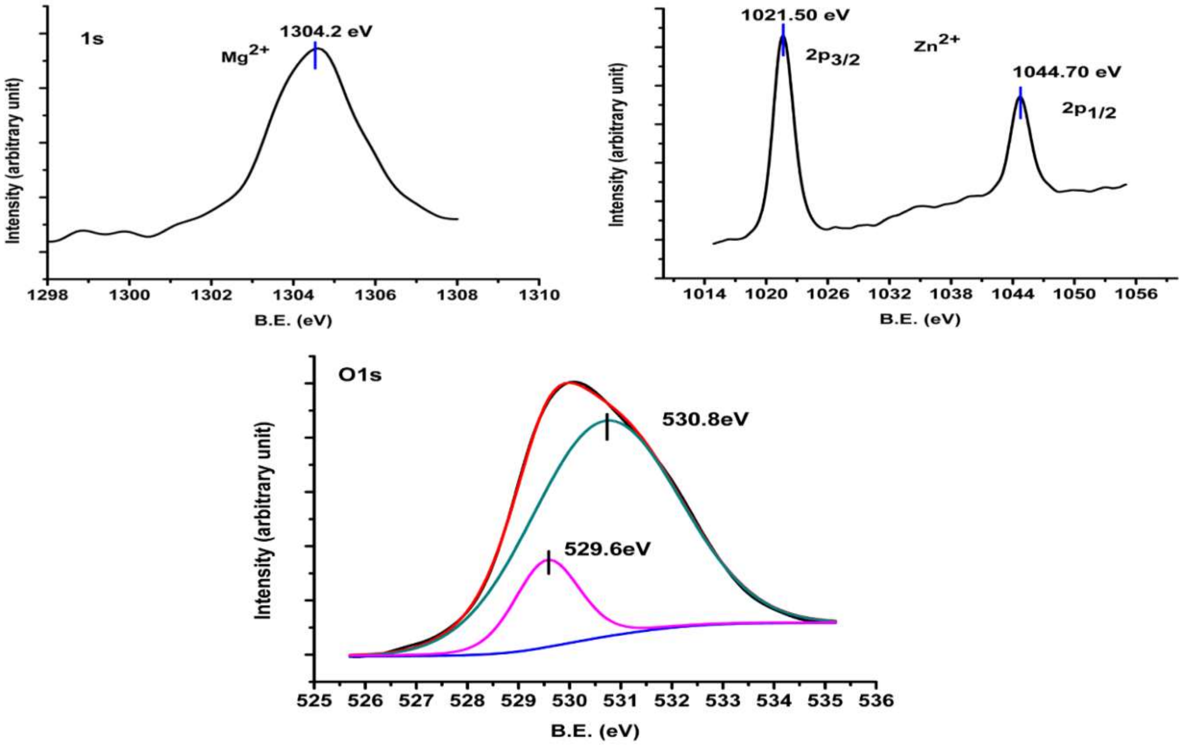


Fig 4.6 XPS spectrum of synthesized 3 wt.% Mg/ZnO catalyst.

4.3.6 Study of Specific surface area and Basicity of synthesized catalyst.

The textrual properties of pure ZnO and Mg doped ZnO calcined at different temperature were studied by Brunauer-Emmett-Teller technique and given in table 4.1. The surface area of pure ZnO was $11.53 m^2g^{-1}$ along with total pore volume $0.1427 cm^3/g$. Both the adsorption and desorption curves were type IV having H1 isotherm hysteresis loop which confirmed the mesoporous nature of the prepared catalyst. Besides this, another factor which classified the mesoporosity of the synthesized catalyst is that the pore diameter values of all the synthesized catalyst calcined at different temperatures fall in the range of 2-50 nm and microporous when > 50nm.The specific surface area as well as pore volume and pore diameter of Mg doped ZnO catalysts increased gradually with increase in calcination temperature which might be due to incorporation and sintering of fine magnesium metals in to the pores of ZnO support which enhanced the mesoporous nature of catalyst providing very effective catalytic activity to synthesized catalyst for trans esterification reaction of glycerol [124,128]. The total basicity and basic strength distribution of the synthesized catalysts calcined at different temperatures were calculated using Hammett indicator test and given in Table 4.1. It is clear from the table that the basicity of 3wt% Mg/ZnO catalyst increases with increase in calcination temperature which facilitate glycerol carbonate synthesis. The conversion of glycerol is highest about 98.4% in case of 3wt%Mg/ZnO calcined at 550^0C as there is creation of strong basic sites of catalyst in comparision to same catalyst calcined at 150^0C and 350^0C due to formation of weak and moderate basic site respectively,where as the 3wt%Mg/ZnO calcined at 750^0C causes less conversion and product yield of glycerol carbonate due to very high basicity which causes decarbonylation of glycerol carbonate to glycidol [129] .

Table 4.1 Properties of synthesized 3 wt% Mg/ZnO catalyst at different calcination temperature.

Catalyst	**Basicity (mmol/g)**	**Surface area (m^2/g)**	**Pore volume (cm^3/g)**	**Pore size (nm)**
ZnO	3.83	11.53	0.1427	21.95
3wt%Mg/ZnO @150°C	4.26	14.45	0.1924	13.92
3wt% Mg/ZnO@350°C	6.76	16.02	0.3781	14.12

3wt% Mg/ZnO@550°C	8.43	19.57	0.6384	17.01
3wt%Mg/ZnO@750°C	11.46	8.97	0.0632	9.73

4.4 Evaluation of catalyst for glycerol carbonate synthesis

The transesterification reaction of glycerol with dimethyl carbonate was carried out in a round bottom flask fixed with a reflux condenser at normal atmospheric pressure. The molar ratio of glycerol to dimethyl carbonate was kept 1:4 with catalyst loading (3wt % of glycerol used) at the optimum temperature of 80°C for 2h. The resultant product mixture was separated by centrifugation after completion of the reaction and analysed by using capillary column HP-5 (30m x 0.32 mm x 0.25 µm) through gas chromatograph Agilent Technologies 7890B equipped with flame ionization detector (FID) with a split injection mode. The operating temperature of the injector and detector were kept 220°C and 300°C respectively. The starting temperature of the oven was kept 40^0C and it was increased at the rate of 10°C/min up to 200°C. The helium gas was used as a carrier gas with the flow rate of 1.7ml/min and the split ratio was 1:80. tertiary butanol was taken as internal standard for GC analysis of synthesized glycerol carbonate. Beside GC analysis,^{1}H NMR, and ^{13}C NMR spectra were also performed for the confirmation of the desired product. Both ^{1}H and ^{13}C NMR spectra of glycerol carbonate is depicted in fig 4.7 as below. After the separation of catalyst from the reaction mixture the by-product methanol obtained was evaporated by rotary evaporator and the synthesized glycerol carbonate undergoes for proton as well as carbon 13 analysis using Bruker Ascend TM 500MHz spectrometer. Dimethyl Sulfoxide–d_6 was used as a solvent and internal reference. The proton NMR spectra of synthesized glycerol carbonate is shown in fig 4.7 (a) and found to be different types of multiplet peaks at different chemical shift values responsible for protons present in the compound. The multiplet peak of chemical shift value of 4.81 ppm is mainly responsible for obtaining the conversion percentage of glycerol-to-glycerol carbonate and can be calculated by the integration area of proton NMR signal at chemical shift of 4.81ppm for methine proton of glycerol carbonate and integration area value for chemical shift of 3.43ppm for methine proton(-CH-) of glycerol [130-131]. From the figure 4.7(b) shown for ^{13}C spectra of glycerol carbonate it was observed that there were four characteristic peaks of glycerol carbonate due to presence of four different carbon atoms, the peak at 155ppm corresponds to carbonate carbon peak of glycerol carbonate including this other three peaks were also observed at 77.09 ppm, 66.46ppm and 60.66ppm for O-CH_2, O-CH and CH_2OH carbon atoms respectively [130]. Another multiplet peak around 40ppm was observed mainly due to deuterated dimethyl sulfoxide (d_6-DMSO). Since there was not complete conversion of glycerol in transesterification processes the other two peaks at chemical shift values 63.42ppm and 72.30ppm corresponded to CH-OH and CH_2-OH carbon atoms of glycerol present in reaction mixture.

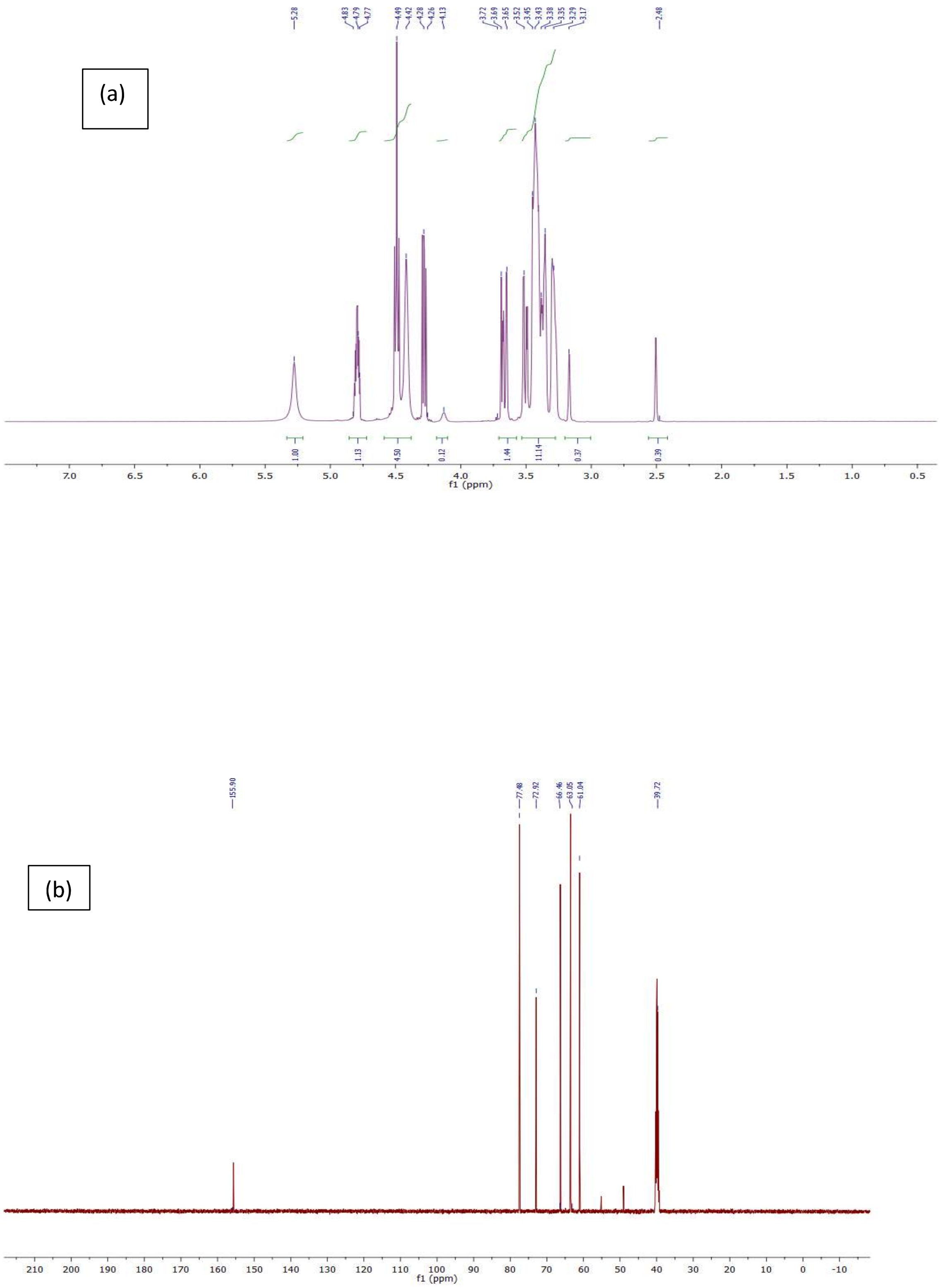


Fig 4.7 (a) ^{1}H NMR spectra (b) ^{13}C spectra of Glycerol carbonate at optimized condition [catalyst dose(3 wt%),DMC to glycerol molar ratio(4:1) at $80^{0}C$ for 2h at stirring speed of 500 rpm

4.5 Detailed study on activity of Mg/ZnO catalyst

The conversion, selectivity and yield of glycerol and glycerol carbonate were obtained by trans-esterification reaction between glycerol and DMC using various types of catalysts and shown in Table 4.2. The basic strength of the catalysts was influenced by metal oxides, (mainly alkali and alkaline earth metal) and increased the catalytic performance in transesterification reaction. Among different catalysts, Mg/ZnO had highest glycerol conversion of 98.4%with GLC selectivity 96.89%. The conversion of glycerol was observed to be low with Mg/ZrO_2 and Ba/ZnO as compared to Mg/ZnO under common reaction conditions. Moreover, the selectivity as well as yield of glycerol carbonate were obtained highest in case of Mg/ZnO as compared to Ba/ZnO, Sr/ZnO, Mg/$ZrO_2$and K/ZnO. Since, magnesium is cost effective and easily available as compared to other alkaline earth metals like Sr, Ba and opted highest conversion as well highest yield so Mg/ZnO was highly preferred as the suitable catalyst for transesterification of glycerol. The plausible reaction pathway for transesterification of glycerol in presence of Mg/ZnO catalyst is represented in fig 4.8 below which follow nucleophilic addition reaction and cyclization to give glycerol carbonate as desired product.

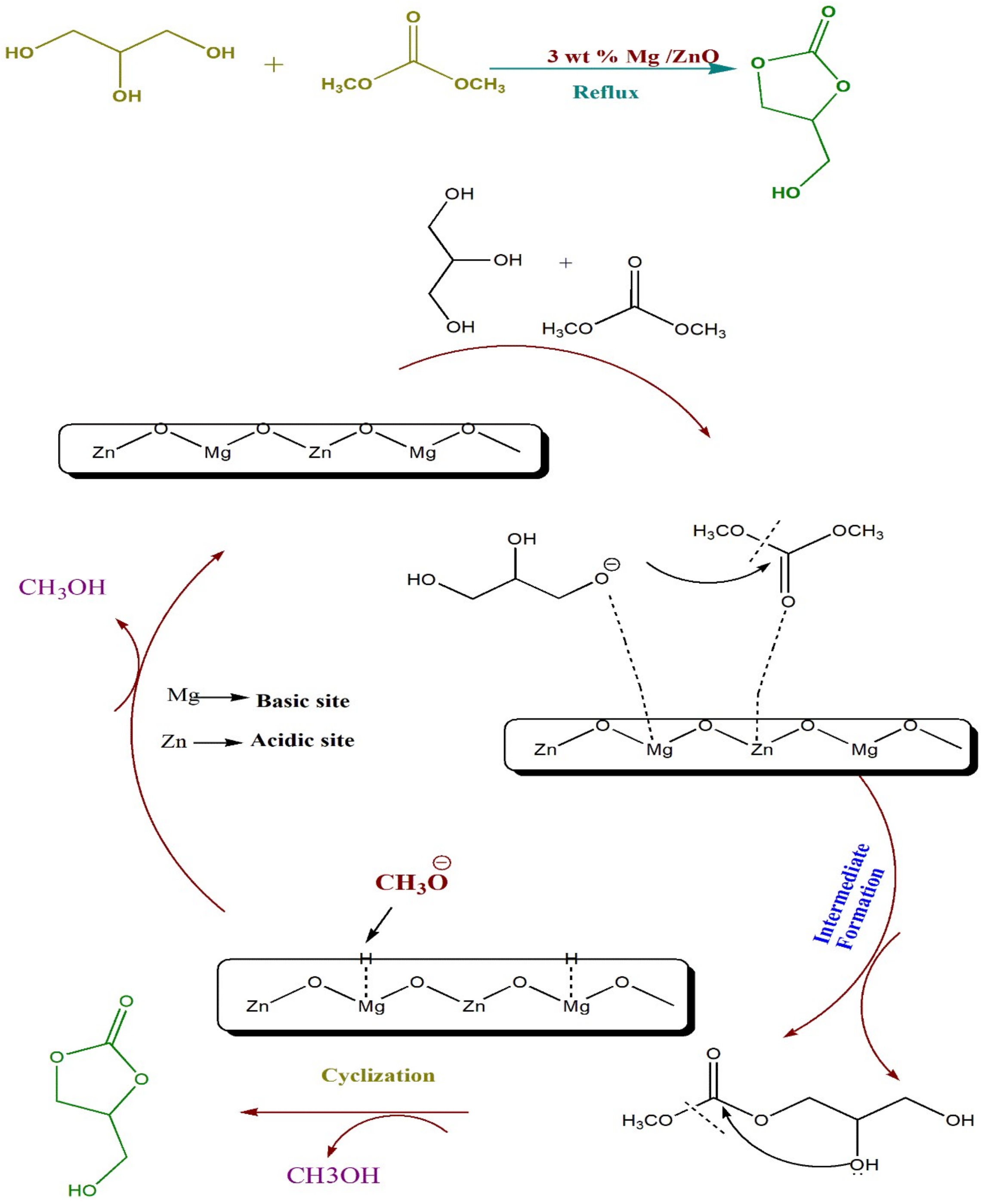


Fig 4.8 Mechanistic path way of Mg/ZnO catalyst in glycerol transesterification with DMC

Table 4.2 Catalyst screening for synthesis of glycerol carbonate

Catalysts	Conversion (%)	GLC selectivity (%)	GD selectivity (%)	GLC yield (%)
Mg/ZrO_2 @550°C	82.36	90.28	9.72	77.55
Mg/ZnO@550°C	98.4	96.89	3.11	90.06
Ba/ZnO@550°C	82.11	92.23	7.77	76.23
Sr/ZnO@550°C	84.77	93.74	6.26	71.48
K/ZnO@550°C	80.63	92.46	7.54	72.07

Including the composition of mixed metal oxides, the 3wt%Mg/ZnO-550 catalyst has better performance in transesterification reaction of glycerol into glycerol carbonate. These were used for the transesterification reaction and are shown in the Table 4.3. The 3 wt.% Mg/ZnO-150 catalyst showed a very low catalytic activity of 17.22% for glycerol conversion and there was a rapid improvement of the catalytic activity with rising calcinations temperature up to 550°C, beyond which the catalytic activity is reduced with further increase of calcination temperature, which might be due to increase of basic strength as well as particle size of the catalyst which affected the catalytic activity of the catalyst. The 3wt%Mg/ZnO catalysts calcined at several temperature have different basic strength values as calculated by Hammet indicator method , the same 3wt% Mg/ZnO catalyst calcined at 550°C provided highest conversion of 98.4% glycerol as the basicity of catalyst was 8.43 mmolg^{-1} with increase in calcinations temperature the basicity increases to higher value which caused decarbonylation of glycerol carbonate into glycidol since higher basic strength prefers for glycidol formation [132-133] . It was concluded that the catalyst procreated at 550°C had best catalytic activity among all the catalysts, with rise in calcinations temperature from 150-550^{0}C the surface area of the used 3wt%Mg ZnO catalyst increased gradually which enhanced the catalytic activity and facilitate transesterification of glycerol by providing stability but at calcinations temperature 750°C the conversion of glycerol decreased since the surface area of the catalyst started decreasing at 750^{0}C due to sintering of metal oxides, which greatly affect the catalytic activity of synthesized 3wt%Mg/ZnO catalyst.

Table 4.3. Effect of Mg loading and catalytic performance of catalysts depending upon calcination temperature.

Catalyst	**Conversion (%)**	**GLC selectivity (%)**	**GD selectivity (%)**	**GLC yield (%)**
ZnO	3.23	93.47	6.53	3.02
MgO	18.72	94.32	5.68	18.15
1wt%Mg/ZnO @550°C	92.44	95.23	6.80	78.35
3wt%Mg/ZnO @550°C	98.40	96.89	1.63	90.06
5wt%Mg/ZnO@550°C	89.27	93.77	6.24	82.79
7wt%Mg/ZnO@550°C	82.44	90.58	9.42	74.33
10wt%Mg/ZnO@550°C	78.89	95.29	4.71	67.46
3wt%Mg/ZnO@150°C	17.22	91.68	8.32	15.28
3wt%Mg/ZnO@350°C	48.27	88.07	12.92	33.11
3wt%Mg/ZnO@750°C	38.67	98.42	1.58	24.22

4.6 Optimization study of reaction parameters.

4.6.1 Effect of Reaction temperature

The 3wt% Mg/ZnO catalyst calcined at 550^{0}C having very good catalytic activity was further investigated for study of reaction parameters and depicted in Fig 4.9 (a). The temperature study of the transesterification reaction of glycerol with dimethyl carbonate greatly influenced the conversion percentage of glycerol. It was observed that the temperature range for the trans-esterification reaction was 65-100°C.At 65°C, the conversion of glycerol was 71% and it was increased up to 98.4% with subsequent rise of temperature up to 80°C.Further increase of temperature beyond 80°C, there was non-significant improvement of product formation which might be due to vaporization of dimethyl carbonate, since the boiling temperature of DMC is 90°C and the temperature higher than 80°C causes creation of three phases of the reaction mixture i.e. glycerol in liquid phase, DMC in gaseous phase and catalyst(Mg/ZnO) in solid phase as a result the conversion percentage of glycerol decreases gradually. Moreover, at higher temperature the decarbonylation of glycerol carbonate leads to formation of glycidol (GD) which badly affected the conversion of glycerol carbonate [134-135] . The conversion of glycerol-to-glycerol carbonate maximized (98.4%) at 80°C due to increase in the mobility of the reacting molecules and further increase of temperature did not influence the product yield as well conversion percentage.

4.6.2 Effect of reaction time

The conversion percentage of glycerol was also influenced by the time of 1to 3h, and it attained maximum conversion of 98.4 % in 2h as shown in fig 4.9 (b). When the reaction time prolonged for 3h, the conversion percentage of glycerol to glycerol carbonate started reducing , although the selectivity of glycidol increased, which might be due to equilibrium in trans-esterification of glycerol carbonate within this time period and beyond that there was appearance of decarbonylation of glycerol carbonate [72]. Since decarbonylation of glycerol carbonate predominates over glycerol, the optimum time period is necessary for obtaining better glycerol carbonate yield.

4.6.3 Effect of DMC to Glycerol molar ratio

During trans-esterification reaction of glycerol with DMC, the conversion as well as product yield was highly influenced by molar ratio of both of the reactants. From fig 4.9(c) As the molar ratio of DMC to glycerol increased the conversion percentage also increased and it maximized up to 98.4% at the molar ratio of 4:1(DMC: Glycerol). Further increase in DMC to glycerol molar ratio did not result either higher conversion or yield percentage. It might be occurred due to the limitation of interaction of base catalyst with the reagent, glycerol and is consequently reduced the conversion of glycerol carbonate [111] . So, it was concluded that the optimum molar ratio of DMC to glycerol :: 4:1 is suitable for transesterification of glycerol-to-glycerol carbonate.

4.6.4 Effect of catalyst loading

The percentage of catalyst loading in the reaction mixture highly affects the conversion and glycerol carbonate yield from the glycerol. With increasing in catalyst loading (on the basis of glycerol weight used,) the product formation takes place in larger quantity and also promotes the reaction rate. From the fig 4.9(d) it is clear that the conversion percentage of glycerol steadily increases from 45% to 98.4% with increase in catalyst loading 1 to 3%(wt.) of glycerol used and above 3wt% loading the glycerol conversion gradually decreases like at 3.5wt% loading it reduced to 76% conversion which might be due to stronger basic sites as the catalyst amount increases in the reaction mixture which helped in decarbonylation of glycerol carbonate and appreciated formation of glycidol .Moreover it was also noticed that with increase in catalyst loading, the deliberate elevation of glycidol(GD) formation. It might be occurred due to the elevation in active basic sites of catalyst by increasing the catalyst loading and it promoted the decarbonylation of glycerol carbonate [78,134,] .

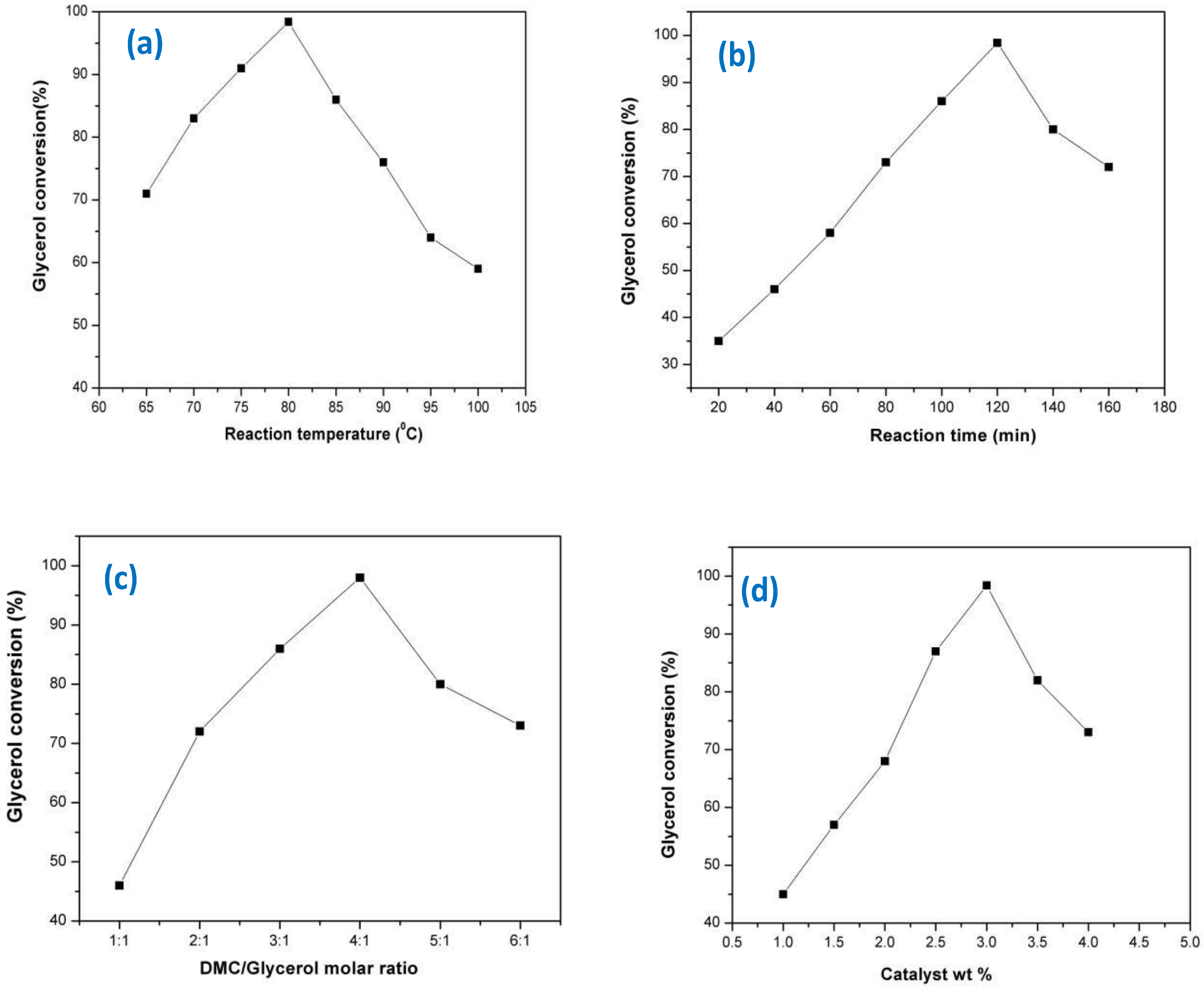


Fig 4.9. Effect of reaction parameters on the glycerol conversion percentage by using 3 wt. % Mg/ZnO catalyst: (a) effect of reaction temperature (b) effect of reaction time (c) effect of DMC/ Glycerol molar (d) effect of catalyst loading weight percentage.

4.6.5 Reusability study of catalyst

In case of catalytic activity study, the reusability of catalyst is essential since it plays vital role in transesterification reaction. The quality of better solid catalyst entrenched its reusability potential. Fig 4.10 represents the reusability of 3 wt.% Mg/ZnO-550 catalyst. After completion of each reaction, the catalyst was separated by centrifugation and washed with methanol for further application. The recovered catalyst was dried in oven and calcined again for the removal of adsorbed organic compounds and used for next run. It was noticed that the catalyst was significantly active up to fifth run giving high conversion of glycerol but during sixth run the conversion of glycerol-to-glycerol carbonate rapidly fell down which might be due to leaching of stronger basic site of catalyst.

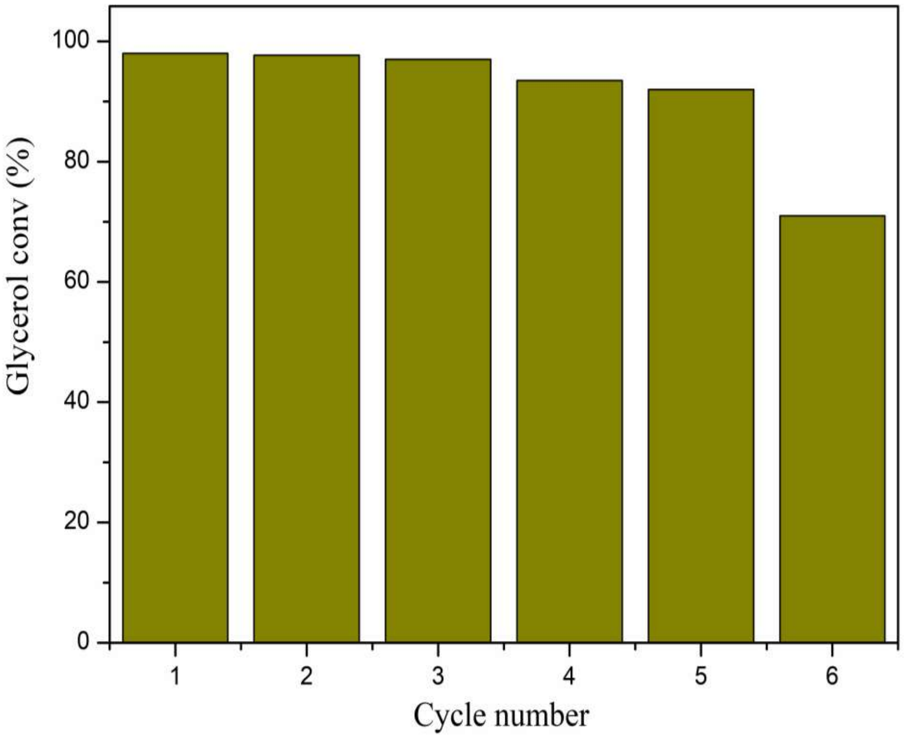


Fig 4.10 Reusability study of 3 wt. % Mg/ZnO catalyst

In order to find out the reason behind the deactivation of catalyst many experiments were performed. To remove the adsorbed particles after completion of reactions, the reused catalyst was calcined for 5h at 550°C, but there was no such type of improvement in conversion and yield also after fourth cycle as given in the Table 4.4. Another test performed was the leaching of active sites of catalyst, which was done by hot filtration procedure. In this method the catalyst was filtered out and the blank reaction was performed for 2h (Entry 5-6). From the result, it was confirmed that the active site leaching of catalyst predominates over adsorbed product species and mainly responsible for the deactivation of catalyst.

Table 4.4 Catalyst deactivation Test

Entry	**Cycle**	**Conversion (%)**	**GLC selectivity (%)**	**GD selectivity (%)**	**GLC yield (%)**
1	1	98.40	98.37	1.73	90.17
2[p]	2	93.57	97.41	2.59	90.03
3[p]	3	90.86	97.77	2.23	89.99
4[p]	4	54.96	100	0.0	54.96
5[r]	5	62.71	95.83	4.17	60.99
6[s]	-	84.23	91.42	8.57	75.66

Reaction conditions; glycerol: DMC molar ratio **4:1**, catalyst:**3 wt%** of glycerol, temperature :**80^{0}C**, time **2h**.

[P] Reused catalyst calcined` at 550^{0}C for 5h

[r] Sample after 1h

[s] After 1h reaction, the blank reaction proceeded for another 2hr.

4.7 Conclusions

This work provided a sustainable approach for synthesis of glycerol carbonate from biodiesel derived waste glycerol using low-cost Mg doped ZnO heterogeneous base catalyst. Among different catalysts, the 3wt%Mg/ZnO calcined at 550°C was one of the best catalysts for transesterification of glycerol. The loading extent of magnesium metal oxide was significantly responsible for strong basic sites of the catalyst which facilitates the reaction rate. During conversion of glycerol, due to decarbonylation of glycerol carbonate another product glycidol was also detected. In case of heterogeneous base catalyst, the catalytic activity is closely related to the basic strength, which mainly dependent on the composition of the catalyst as higher the base strength, higher will be the catalytic activity. All the characterizations like XRD, FT-IR, SEM-EDX, TGA-DSC etc of synthesized 3wt%Mg/ZnO catalyst and quantitative analysis of produced glycerol carbonate was studied through ^{1}H NMR and gas chromatography process. Finally, the limitations of heterogeneous catalysts open avenues and new frontiers to enhance the properties of heterogenous catalysts and develop methods devoid of variations to optimize reaction parameters. The optimized parameters can then be used to alter the carboxylation and acetylation of glycerol with DMC to obtain the desired products, namely, Glycerol carbonate.