Chapter 5

Synthesis of Ni modified distillation waste derived catalyst used to produce glycerol carbonate from biodiesel by-product glycerol

5.1. Introduction

In this chapter, a new heterogeneous catalyst was synthesized utilizing non–toxic, ecofriendly, and greener distillation waste. During the process of distillation, the metal salts present in the liquid or water starts accumulating on the surface of the wall of the distillation compartment in the form of their hydroxides, carbonates, and bicarbonates as solid or semisolid wastes. Normally, Ca and Mg salts are present in tap water, but in our instance, Ca salts predominated, as validated by EDAX analysis, and Mg may have been present in very minute amounts below the instrument detection limit. In this study, distillation waste was modified by nickel nitrate using solid-state synthesis, coprecipitation, hydrothermal, and wetness impregnation methods. The comparative study of the catalyst obtained from the above methods is also studied. The primary purpose of synthesizing the mixed metal oxides was to improve their physicochemical properties and catalytic activity toward producing glycerol carbonate. Transition metal oxides, such as nickel oxide and others, have been previously discovered to operate as a co-catalyst due to qualities such as changeable oxidation state, high catalytic efficiency, ion complex formation, and high catalytic stability. Moreover, NiO shows significant catalytic activity among different transition metals due to its affinity toward oxygen and received substantial attention in various areas due to its important optical, magnetic, and electrical properties. To the best of our knowledge, the transesterification of glycerol using distillation waste modified by NiO catalyst for the manufacture of GlyC has not been explored. In order to produce pure and quantified glycerol carbonate, the influence of various factors (such as synthesis method, calcination temperature, and the ratio of element loading) and the effect of different reaction parameters were also investigated.

5.2. Synthesis of Ni/CaO catalyst

At first, CaO nanoparticles were synthesized by using distillation waste. The procured distillation waste was centrifuged and washed several times with double distilled water and

ethanol to get the pure raw material. The obtained residue was dried in an oven for 12 hours and crushed using mortar pastel to get the raw material to prepare the catalyst. The obtained material was further undergone for the thermal treatment and calcined at 800 ℃ for 4 hours. After that the sample was taken and again ground to further use as the CaO precursor material. Now, the calcinated distillation waste was doped with nickel oxide to prepare the target catalyst. Ni-modified distillation waste (CaO) based heterogeneous catalyst Ni/CaO (NDW) was prepared through a wet impregnation process and used for transesterification. This Ni-modified distillation waste-based catalyst was denoted as NDW. In order to investigate the role of the catalyst synthesis procedure on the phase and activity of the NDW catalyst, the catalysts as mentioned above, were synthesized by the wetness impregnation method. Initially, the catalyst was synthesized taking a 2:1 Ni/Ca atomic ratio respectively, named NDW. The obtained catalyst undergoes calcination at 700 and 900 ℃ to get the product named NDW@700 and NDW@900, respectively. The synthetic procedure of NDW catalyst is shown in Figure 5.1. The catalyst stability was checked by performing different characterization techniques, and the catalyst performance was tested through a transesterification reaction of glycerol [152].

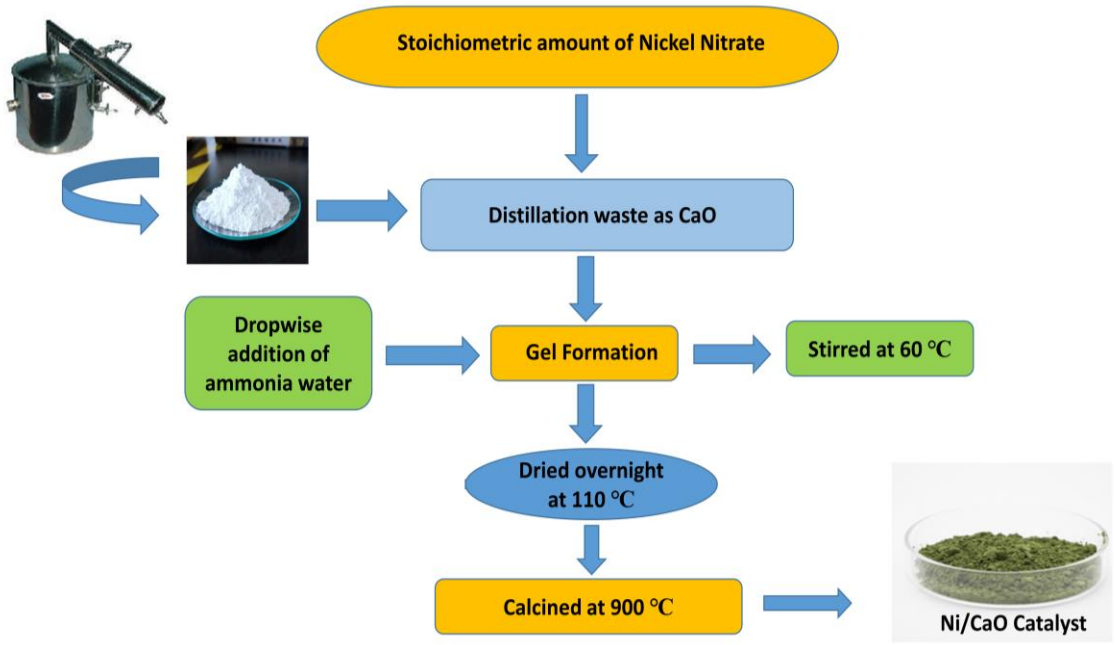


Figure 5.1 Flow chart for synthesis of Ni/CaO catalyst.

5.3. Characterization of the catalyst

5.3.1. TGA & DSC studies

The thermo-gravimetric studies ascertained the thermal and structural stability of the synthesized NDW catalyst. Figure. 5.2 displays the TG-DSC profile of NDW catalyst, which exhibits two regions of weight loss. The first stage of weight loss, i.e., 3.94%, was seen at temperatures 0 – 100 ℃, attributed to the loss of surface adsorbed moisture present on the surface of NDW. In the second stage of weight loss, i.e., 25.11% observed around 250 -550 ℃ concerned with breaking and forming the bond between Ca and Ni and Oxygen. None of the weight loss are witnessed after 550 ℃ indicates that the catalyst is stable above 550 ℃. DSC curves show the endothermic nature of the weight loss process. The endothermic heat flow corresponding to the second weight-loss stage is 388.21 J/g. Thus, TG-DSC studies show that the catalyst is stable above 550 ℃, and the weight loss of the catalyst before the stable temperature is endothermic [152].

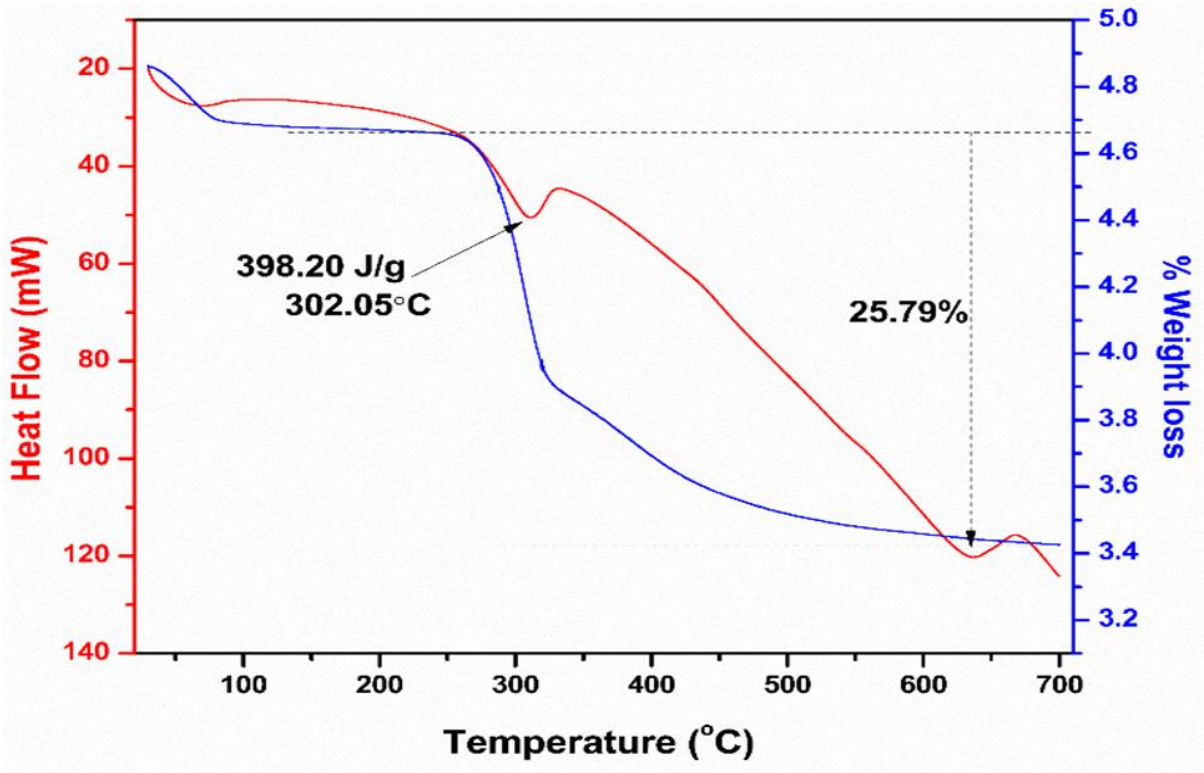


Figure 5.2 TGA – DSC plot of NDW catalyst (without calcination).

5.3.2. XRD studies

Figure. 5.3 enumerated the XRD diffractogram of raw distillation waste, calcined distillation waste, and Ni-doped distillation waste calcined at 700 ℃ and 900 ℃, respectively named DW, calc. DW, NDW@700, and NDW@900. From the figure, all the synthesized catalysts exhibit intense and crystalline peaks of CaO phases and Nickel-metal oxide phases. The XRD patterns of the obtained distillation waste, i.e., DW, show that the $CaCO_3$ phase appeared at 2theta values equal to 23.42, 29.52, 43.299, 47.68, 63.01 at hkl plane, respectively. On calcining the raw distillation waste, the carbonate peaks converted into cubic CaO phase showed at 2theta equals to 37.38, 53.83, 32.12, 64.15, 67.40, having hkl planes viewed at (200), (220), (111), (311) and (222) respectively in accordance with JCPDS database 77-2376. Due to absorption of ambient oxygen on a crystal lattice, some minor peaks of $Ca(OH)_2$ also appeared at 2theta equal to 34.15, 50.88, 28.73 corresponding to (101), (110), (100) hkl planes, respectively matched with JCPDS file no. 44-1481. The Ni-loaded CaO catalyst calcined at 700 and 900 ℃ showed a similar diffraction pattern with some new peaks of NiO appearing at 2theta equal to 37.3, 43.3, 62.8 consisting (200), (111), (220) hkl planes respectively in accordance to JCPDS file no. 73-1523. However, the catalyst calcined at 700 ℃ contains some peaks of $CaCO_3$ and $Ca(OH)_2$, which interfere with the catalytic performance, whereas the catalyst calcined at 900 ℃ shows only peaks of NiO and CaO pure phases. Also, the diffraction peak at 37.3 corresponds to NiO and CaO, an overlapping peak for both cubic phases [153].

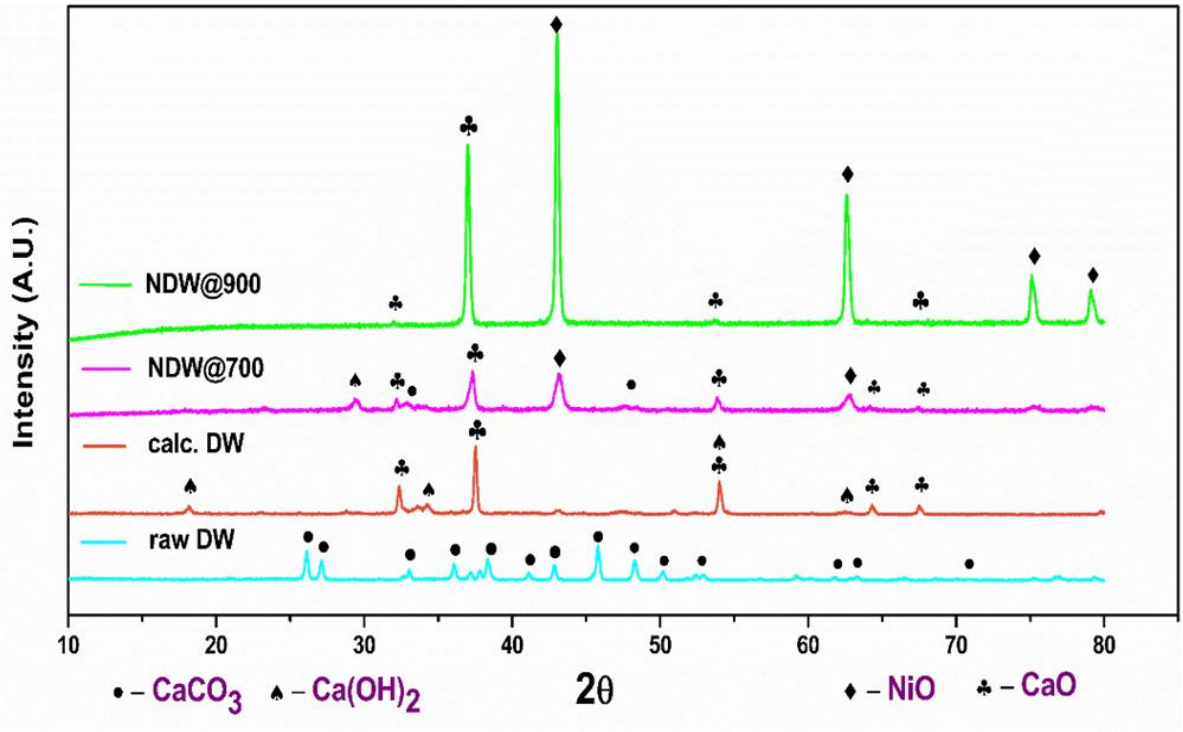


Figure 5.3 XRD spectra of raw distillation waste (DW), calcined DW, NDW catalyst calcined at 700 ℃, and NDW catalyst calcined at 900 ℃ respectively.

5.3.3. FT-IR studies

The FT-IR spectra of different DW-based catalysts depicted in as Figure. 5.4. The presence of a low-frequency vibration band at 588.56 cm^{-1} is due to the O-Ti-O group [154]. The absorbance band situated at ~ 878 cm^{-1} is attributed to O-Ni-O-Ca-O bond vibrations, which approve the formation of mixed metal oxide. The peak originated at ~ 1474 cm^{-1} and indicates the presence of carbonate ion within the interlayer region due to absorption of atmospheric carbon dioxide. Carbonate peaks are observed when the catalyst was calcined at 700 ℃, i.e., CN700. The vibration band diminishes rapidly when the thermal treatment of the NDW catalyst increases from 700 to 900 ℃ (CN900). In all IR spectra, the stretching vibrations from ~3648 cm^{-1} can be owed to the existence of hydrogen linked to the surface Ni group, surface hydroxyl group, i.e., $Ca(OH)_2$, and captured water molecules on the surface of the catalyst [155]. The hydroxyl stretching frequency diminished with increasing calcination temperature to 900 ℃.

The above characteristics were evident in forming new metal and O bond of O-Ni-O-Ca-O contained by the crystal lattice. The findings are consistent with the XRD data.

FT-IR studies also explored the effect of the synthesis procedure on the nature of the functional group present on the surface of the catalyst. Metal carbonate vibrations reveal the synthesized catalyst's stability and proceed through the wetness impregnation method. The effect of the synthesis procedure can be seen in the conversion of glycerol. It was found that the NDW catalyst synthesized through the wetness impregnation method gives the highest conversion and selectivity towards glycerol carbonate products. Other methods like coprecipitation, solid-state synthesis, and hydrothermal method synthesis gives lower conversion % of glycerol. This is due to the formation of inactive metal carbonates due to the absorption of ambient carbon dioxide, which restricts the transesterification reaction to form glycerol carbonate.

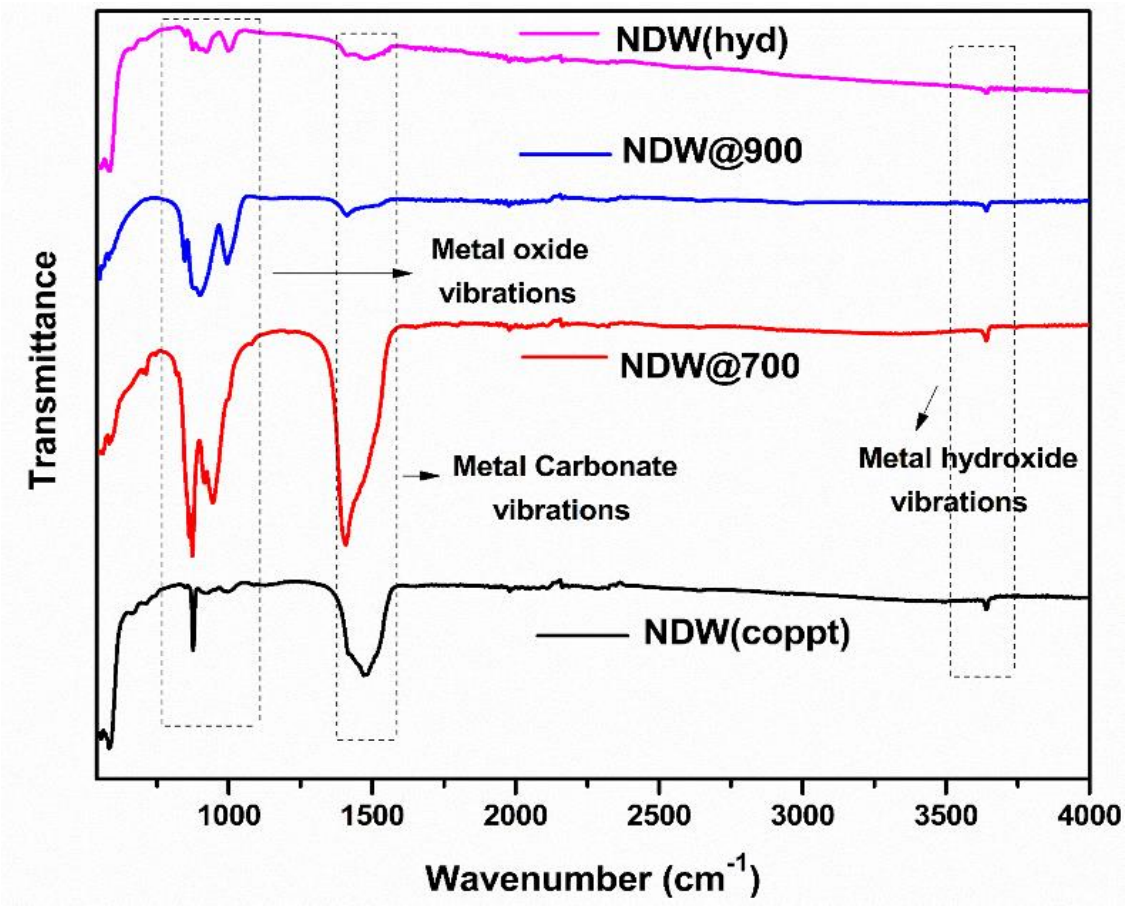


Figure 5.4: FT-IR spectra of NDW synthesised by coprecipitation method, NDW calcined at 700 ℃, NDW calcined at 900 ℃, and NDW synthesised by hydrothermal method.

5.3.4. XPS analysis

The XPS survey spectra of NDW catalyst displayed in Figure. 5.5. The spectra displayed the presence of all three elements, viz. Ca, Ni, and O as their constituents above the detection limit. The binding energy of different elements present in NDW catalyst was estimated taking C1s as reference. The Ca2p spectra show the formation of a doublet viz. $2p_{1/2}$ at 350.42 eV binding energy and $2p_{3/2}$ at 346.94 eV binding energy components separated by 3.54 eV arises due to spin-orbit coupling. The Ni2p spectra also form two doublets (four peaks) of $Ni2p_{1/2}$, $Ni2p_{3/2}$, and their corresponding satellite peaks. The $Ni2p_{3/2}$ peak was further deconvoluted into their subcomponents which may correspond to the two crystallographic distinct components of Ni^{+2} and Ni^{+3} that appeared at binding energy 853.32 eV, 855.43 eV, respectively. Also, $Ni2p_{1/2}$ deconvoluted into its corresponding +2 and +3 crystallographic components having a binding energy of 870.77 eV and 872.68 eV, respectively. The O1s spectra contain two peaks at 528.85 eV due to the formation of metal oxides and the other at 531.04 eV attributed to the formation of metal carbonates due to absorption of ambient air, respectively [113]. The studies agree with the NIST and Thermo fisher XPS databases.

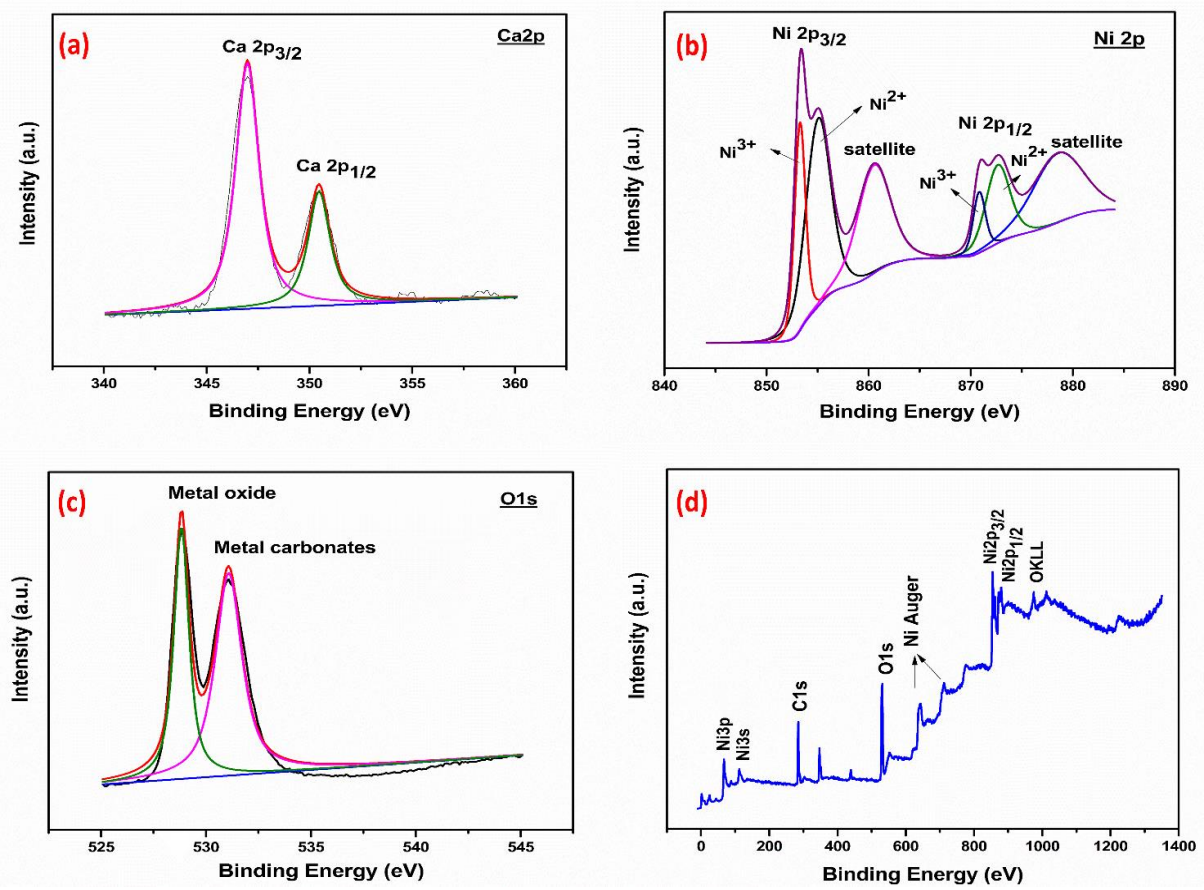


Figure 5.5. XPS spectra of (a) Ca2p, (b) Ni2p, (c) O1s and (d) XPS survey spectra of all the elements present in NDW catslyst**.**

5.3.5. SEM analysis

The SEM micrographs of NDW catalysts is shown in Figure. 5.6**.** The micrographs portray the irregular-shaped particles on the catalyst's surface with varied grain sizes. In the micrograph, NDW catalyst calcined at 900 ℃ displayed the formation of an irregular spheroid and rod-shaped particles with sizes around 28.65 nm. The smaller grain size could offer greater surface area, further boosting the catalytic proficiency. Some particles were aggregated to form agglomerates with different grain sizes disseminated on the catalyst's surface [152]. The EDAX study evident the existence of Ca, Ni, and O atom on the catalyst's surface. The elemental composition of different elements confirmed the weight percentage of the mixed metal oxide catalyst. From the EDAX report, it can be ascertained that the atomic % and weight % of Ca are high in the catalyst, confirming the formation of a 2:1 stoichiometric of Ca and Ni in the

NDW catalyst. The EDAX is illustrated in Figure. 5.6. It can be concluded that the synthesized catalyst does not contain any contaminations. It only contains Ca, Ni, and O elements. The results are in agreement with XRD studies.

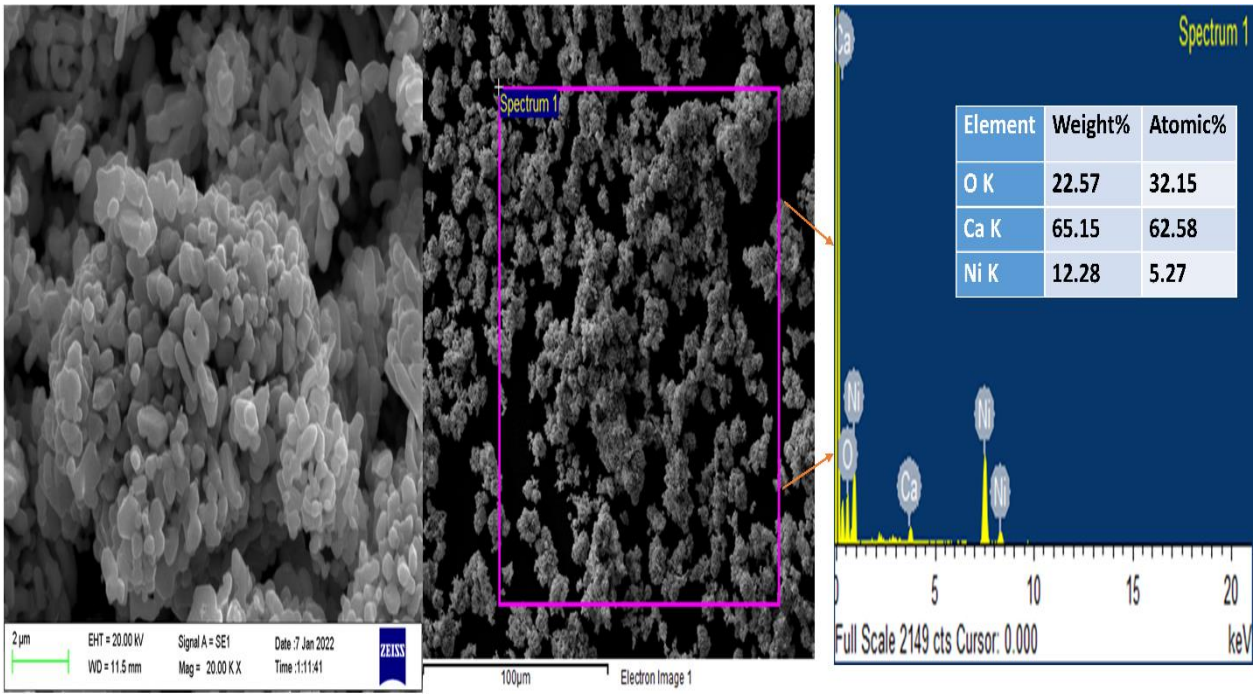


Figure 5.6. SEM images of NDW catalyst and EDAX spectra of NDW.

5.3.6. TEM Studies

TEM images shows the inside arrangement of the particle in the catalyst. It displays the presence of two types of particles which confirms the impregnation of Ca over the nickel surface. The crystalline particles are spherical, having varied sizes ranging from 10.21 to 53.4 nm. The average particle size shown by the histogram in as Figure. 5.7 comes to be 25.68 nm. The nano size of the particles facilitates the catalyst activity. The SAED pattern displays different rings that show the crystalline nature of the catalyst [153]. The dots present on different circular rings indicate the synthesized catalyst's crystal planes, which accorded with the JCPDS file. Therefore, the results are in agreement with XRD and SEM results.

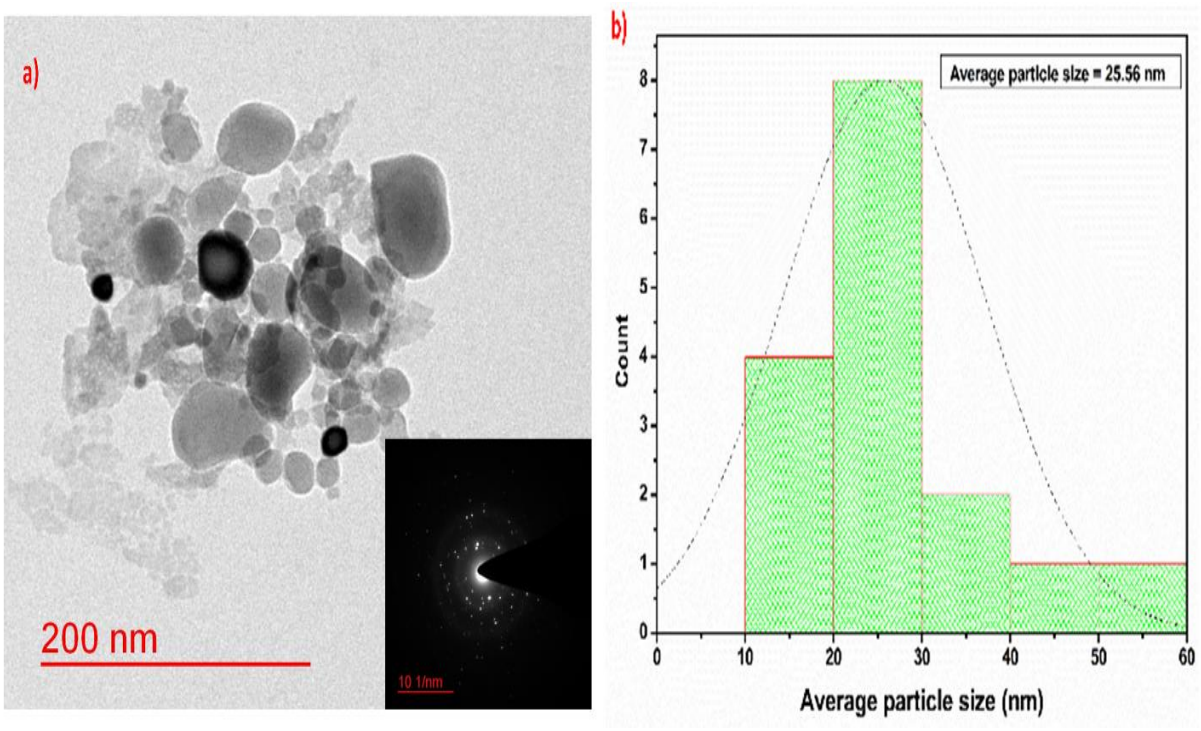


Figure 5.7: (a) TEM micrographs of synthesised NDW catalyst; (b) Histogram showing average particle size

5.3.7. Basicity

Basic strength and number of basic sites present in the heterogeneous catalyst play a key part in the transesterification reaction of Glycerol to produce the product GlyC. To study the basicity and obtain the basic strength of the NDW catalyst, Hammett indicator titrations tests have been performed. The obtained results are presented below. In this titration method, different indicators within pH range 7 to 18 were taken like bromothymol blue with H_ =7.2, phenolphthalein with H_ = 9.8, 2,4- dinitroaniline with H_ = 15, 4-nitroaniline with H_ = 18.4. During the titration, 25 milligrams of synthesized catalyst were mixed with 1.0 cm^3 of Hammett indicator solution, which was diluted with methanol and kept aside to equilibrate for 2 hours. After a definite time, interval, a change in color of the indicator solution was observed, inferring the strong basic nature of the catalyst than the indicator. The quantitative analysis of basicity was determined by benzene carboxylic acid Hammett indicator titration. The basic strength of raw distillation waste i.e., DW, comes from $9.3 < H_ < 15$, which exhibits low basic strength

and consists of 33.42 mmol/g of basic sites. On mixing both the precursors, the basic strength of the 1:2 Ca/Ni catalyst comes in 9.3<H_< 15. But, as the stoichiometric ratio of Ca increases to 2, i.e., 2:1 Ca/Ni (2:1 NDW), basic strength is improved and falls in the desired region i.e., 15< H_ <18.4, and the amount of basic sites comes in the range of 35.65 mmol/g which is appropriate for the synthesis of product GlyC. A higher amount of Ca increases the basic strength, leading to decarboxylation of the glycerol carbonate and decreasing glycerol carbonate yield. Therefore, 2:1 NDW thermally treated at 900 ℃ exhibits the best activity among other catalysts [152].

5.4. Evaluation of the catalyst for glycerol carbonate synthesis via transesterification

The evaluation of catalyst for glycerol transesterification was executed in a two-neck flask of 150 mL capacity fitted with a refluxing condenser. The setup was immersed in silicone oil bath to maintain the temperature. The whole batch reactor system was placed on a spinot magnetic stirrer. In the typical experiment, 9.2 g of glycerol and 1.80 g of DMC were stirred along with 0.46 g of catalyst. The reactants are set to mixing at 600 rpm briskly till the reaction temperature is set at 90 ℃. The reaction was operated for 2 hours for the preliminary test applying the aforementioned reaction conditions. After 2 hours, the reaction mixtures were taken out and centrifuged to obtain the liquid compound. Further, the liquid compound underwent rotatory evaporation to get the purified glycerol carbonate. After the reaction, the recovered catalyst NDW was washed with ethanol 2 to 4 times and dried up at 100 ℃ in an oven for further utilization of the catalyst. The obtained compound was undergone for ^{1}H and ^{13}C NMR analysis to ascertain the formation of glycerol carbonate [156]. The composition of the reactants and products involved in the transesterification reaction was confirmed by performing an HR-MS analysis. The TOF of the synthesized catalyst is calculated and comes out to be 9.74 h^{-1}. This demonstrates the noticeable activity of the synthesized catalyst towards the glycerol conversion to glycerol carbonate.

5.4.1. ^{1}H- NMR and ^{13}C-NMR

The synthesized glycerol carbonate was characterized by ^{1}H NMR spectroscopy to examine the product's proton profile. The NMR spectra are shown below in Figure. 5.8 (a) and (b). Figure 5.8 (a), exemplified the proton NMR spectra consisting of the characteristic's peaks of methine proton at 4.8 ppm, which governed the glycerol conversion during the transesterification reaction. The extent of glycerol conversion was calculated by proportionating the integral value of methine proton of dioxane ring emerged at 4.8 ppm. The peak that emerged at 5.2 ppm indicates the hydroxyl group present in the ring. Other signals represent the respective protons present in the ring. The peak that emerged at 3.31 ppm revealed the presence of methanol in the product, which is to be removed using a rotatory evaporator. The peak that emerged at 2.5 ppm indicates the DMSO–d_6 solvent peak. Thus, the conversion % of glycerol was quantified to be 99.2%, determined by using the integration peak of methine proton at 4.8 ppm using equation 2.1. Figure. 5.8(b) exemplifies the carbon NMR spectrum of synthesized glycerol carbonate. The prominent characteristic peaks appeared at 61.1, 66.4, 77.5, and 155.74 ppm representing the carbon atoms present in glycerol carbonate moiety. Additionally, extra peaks that appeared at 49 and 40 ppm are associated with the methanol and DMSO – d_6 solvent, respectively. This validates the formation of the glycerol carbonate as a product [157].

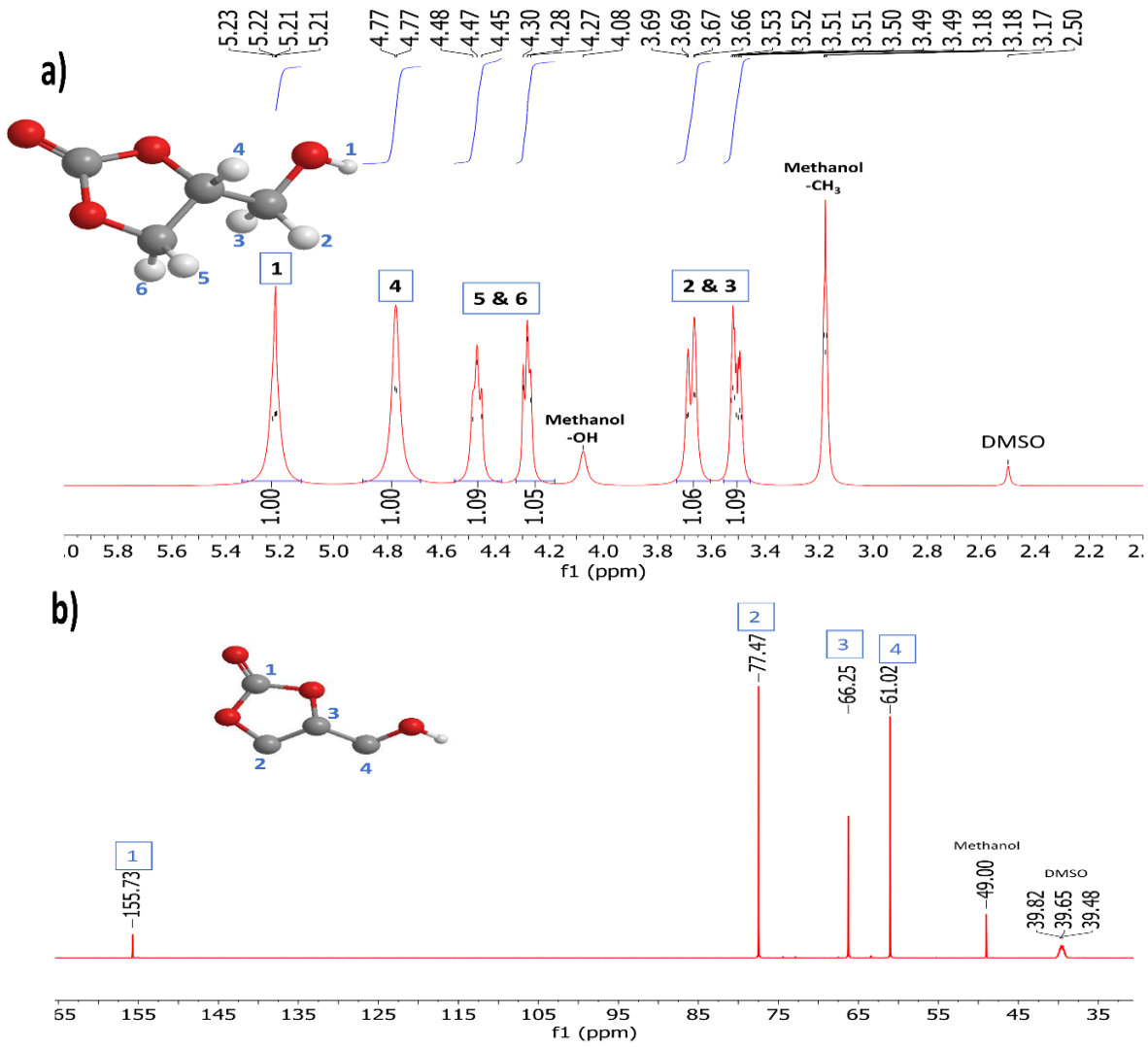


Figure 5.8. (a) ^{1}H-NMR spectra of products, and (b) ^{13}C NMR spectra of product.

5.4.2. HR-MS studies

The composition of reactants involved in the reaction and the product formed can be evident through high-resolution mass spectroscopy (HR-MS) studies shown in supporting information as Figure 5.9 (a) and (b). The components before and after the glycerol transesterification reaction present in the reaction mixture were analysed in this study. Based on HRMS studies of obtained product, it is evident that catalyst is highly selective for glycerol carbonate as there is no peak for glycidol which is observed around 75.02 m/z [156]. Also, there is complete conversion of Gly-to-GlyC as glycerol peak (93.05 m/z) is absent in HRMS spectra of product, which can be further supported by NMR studies.

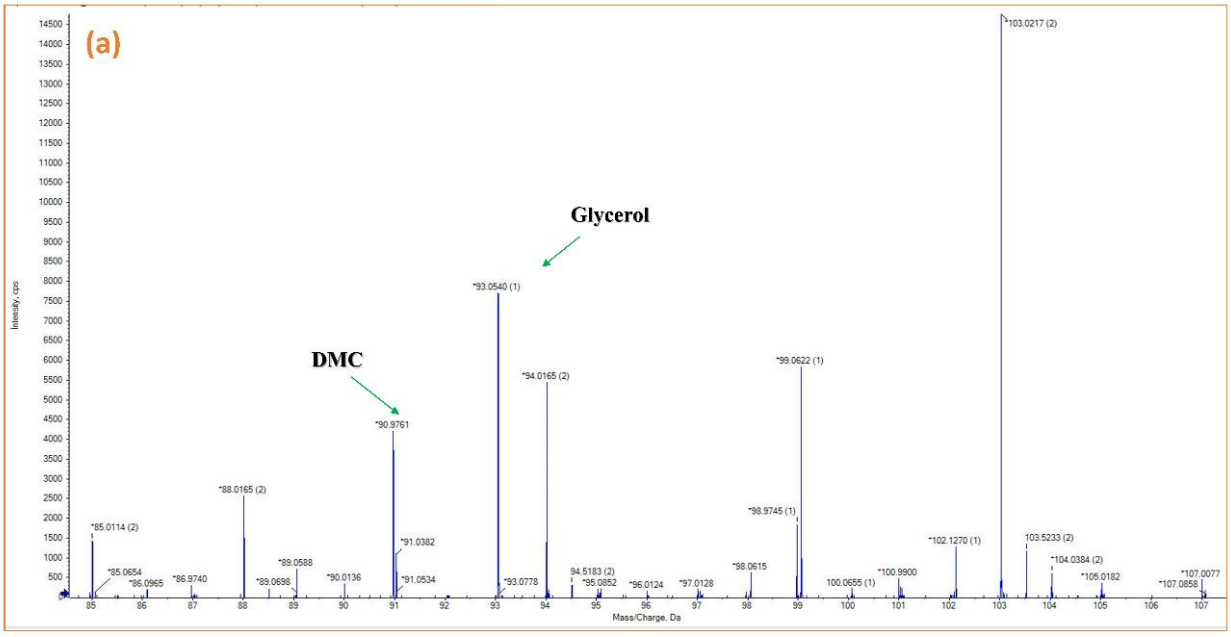


Figure 5.9 (a). HRMS spectra before the reaction.

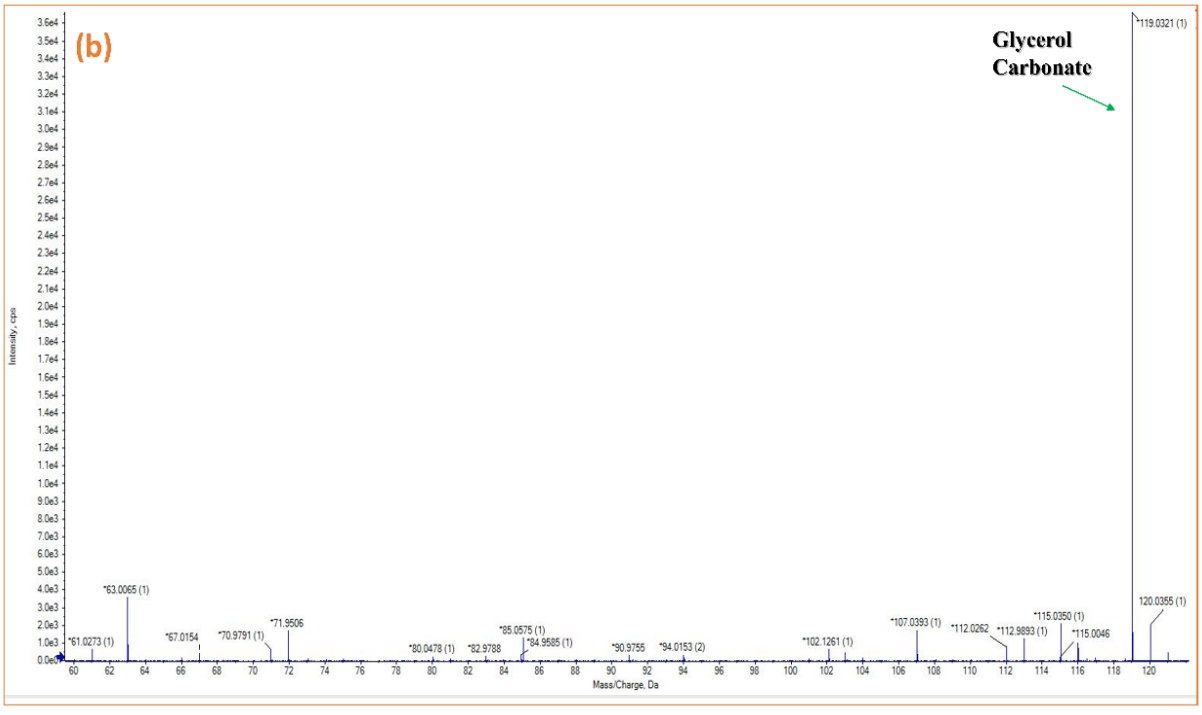
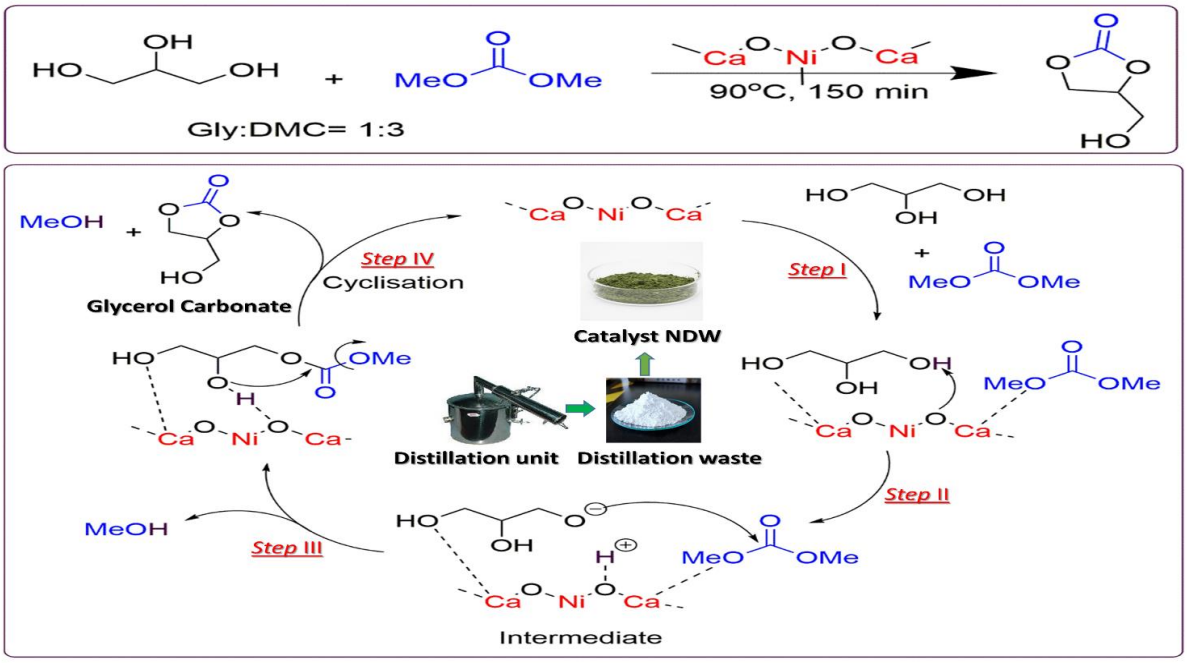


Figure 5.9 (b). HR-MS spectra of componenets after the reaction.

5.5. Proposed mechanism for transesterification of the product

The transesterification reaction of glycerol to produce GlyC is represented in **Scheme 5.1**. The hypothesized reaction process follows the LHHW mechanism, which supports the reaction mechanisms catalyzed by heterogeneous catalysts. At first, glycerol and DMC molecules diffuse towards the surface of the catalyst and then adsorb into the catalyst pores. The glycerol molecule was deprotonated by the NDW catalyst's basic site i.e., CaO and thus its nucleophilicity is increased. The carbonyl carbon's electrophilicity is increased through its coordination with the acidic Ni-O core. After this, the deprotonated glyceroxide molecule attacks the carbonyl carbon and an intermediate is formed. This formed intermediate undergoes intramolecular cyclization utilizing 2^0 OH group of glycerol. Subsequently, the methanol molecule departs and glycerol carbonate is produced finally. The desorption of formed products from the catalyst surface to the bulk phase occurs. These processes produce GlyC and methanol, respectively. The above-discussed mechanism is also supported by many previous studies [158].



Scheme 5.1. Proposed reaction mechanism presenting the role of NDW catalyst in transesterification reaction.

5.6. Effect of reaction parameters on product yields

After synthesizing the catalyst and studying its physicochemical properties, the catalyst was undergone for the transesterification of glycerol to produce GlyC. In order to obtain the maximum conversion of glycerol towards GlyC, different reaction constraints were optimized. These parameters include catalyst dose in the reaction mixture, reaction temperature, molar ratio of glycerol to DMC, and reaction time. The optimization was done using one parameter varied at a time (OVAT) method.

5.6.1. Catalyst amount

The impact of catalyst amount on the formation of GlyC was studied and illustrated in Figure. 5.10(a). The catalyst amount in transesterification reaction varied from 100 mg to 500 mg with respect to the weight of glycerol taken in the reaction medium. The other parameters were kept constant. It was observed that the catalyst amount considerably affected the glycerol carbonate formation. On taking a lower catalyst amount, i.e. 100 mg, a lesser conversion of 65 % is obtained. The increase in catalyst amount to 300 mg increases the glycerol conversion to 99.2 % due to an increase in the number of available active sites required to react to the glycerol and DMC molecules. During the transesterification of glycerol with DMC, the catalyst's active sites and basic strength are closely correlated with its activity. A high GlyC yield cannot be achieved with a lower catalyst concentration since there aren't enough active sites available. A greater number of active sites were made available for transesterification as a result of the high catalyst concentration in the reaction matrix, making it simpler to reach the active sites and accelerating transesterification. However, a further increase in the catalyst concentration to 500 mg would cause agglomeration and mass transfer resistance between the DMC-glycerol-catalyst phases, which would result in decreased glycerol conversion. This could be attributed to insufficient catalyst dispersion in the reaction media [159]. Therefore, the catalyst amount of 300 mg is optimum for the highest conversion of glycerol to GlyC.

A biphasic system arises in the reaction media during the glycerol transesterification reaction as a result of the hydrophilic nature of glycerol and the hydrophobic nature of DMC. The immiscibility of two reactants causes a mass transfer resistance in the reaction matrix, which has an impact on the transesterification reaction. Additionally, the increased catalyst loading would also cause agglomeration and mass transfer resistance between the DMC-glycerol-catalyst phases and result in decreased glycerol conversion. This is attributed to the reaction medium's insufficient ability to disperse the catalyst. Due to the immiscibility of the reactants caused by the presence of two liquid phases at the beginning of the reaction and the catalyst, there is an external mass transfer constraint at lower stirring speeds. Increasing the reaction's stirring speed makes it possible to overcome the catalyst's external mass transfer constraints. However, in our case, we have performed the transesterification at a stirring speed of 700 and beyond so that the external mass transfer limitation is mitigated and did not interfere with the conversion of glycerol. [160]

5.6.2. Reaction temperature

The impact of reaction temperature on GlyC yield was explored by altering the reaction temperature from 60 ℃ to 95 ℃ by upholding the other parameters remains constant. The effect of reaction temperature on the conversion of glycerol is shown in Figure 5.10(b). On operating the reaction at 65 ℃, a lower conversion rate, i.e., only 35 %, was observed. The number of collisions between reactant molecules increases (according to collision theory). The conversion amplified as the temperature rose from 65 ℃ to 85 ℃, 86 ℃. The maximum conversion of glycerol was observed at 90 ℃, which is 99.2 %. Above 90 ℃ the number of DMC molecules in the reaction phase (liquid phase) decreases drastically due to the increased rate of vaporization of DMC (B.P. 90 ℃), as a result, the availability of DMC molecules in the reaction matrix (liquid phase) decreases that causes of the reduction in glycerol conversion above 90°C. This also led to the formation of three phasic mixtures (solid phase of the catalyst,

liquid phase of glycerol, and vapour phase of DMC molecules), and thus the quantity of reactant molecules is reduced, which in turn reduces the effective collisions between glycerol and DMC. Consequently, yield also decreases [161]. This decreases glycerol yield above 90 ℃. Hence, 90 ℃ is found as an optimized reaction temperature. Also, the yield of glycerol carbonate was affected at elevated temperatures to 95 ℃ due to the formation of glycidol, which agrees with the previous reports.

5.6.3. Molar ratio

The impact of the molar ratio of GlyC yield was explored by altering the glycerol to DMC molar ratio starting from 1 to 7 shown in Figure 5.10(c). At equimolar concentration, a lower conversion of glycerol is obtained, i.e., only 65% can be converted to glycerol carbonate as glycerol is slightly miscible in DMC, so the excess of DMC is prerequisite to facilitate the reaction in the forward direction. On increasing the volume of DMC, the reaction shifted towards the forward direction, and conversion increased to 72 % at 1:2 glycerol to DMC. The conversion of glycerol was affected by increasing DMC concentration which facilitates shifting the equilibrium forward [162]. The highest conversion was achieved at a 1:3 molar ratio of 99.2 %. Further, on increasing the molar ratio to 7 mmol of DMC, the conversion of glycerol decreases to 52 %. This is due to the formation of diglycerol carbonate because of the attack of free –OH group of glycerol carbonate on excess of DMC.

5.6.4. Reaction time

The impact of reaction time on GlyC conversion and selectivity were studied and illustrated in Figure 5.10(d). The conversion for the transesterification reaction was monitored for up to 240 min at different time intervals. The selectivity effects with an upsurge in reaction time. At 30 min span, the conversion achieved was only 42 %. With increasing time, the conversion of glycerol increases to 83 % at 75 mins. The maximum conversion obtained is 99.2 % at 90 mins. At the optimized reaction time, the equilibrium of the reaction has reached and as the time

increases the selectivity towards glycerol carbonates decreases as the reaction favours decarboxylation and formation of glycidol. Consequently, the yield of glycerol carbonate starts decreasing above 90 min. This scenario shows that the number of available basic sites favours the decarboxylation of GlyC to form glycidol [163]. Therefore, the conversion and selectivity decrease after a certain point in time. The reaction stopped after 90 min to achieve the maximum conversion and selectivity towards glycerol carbonate.

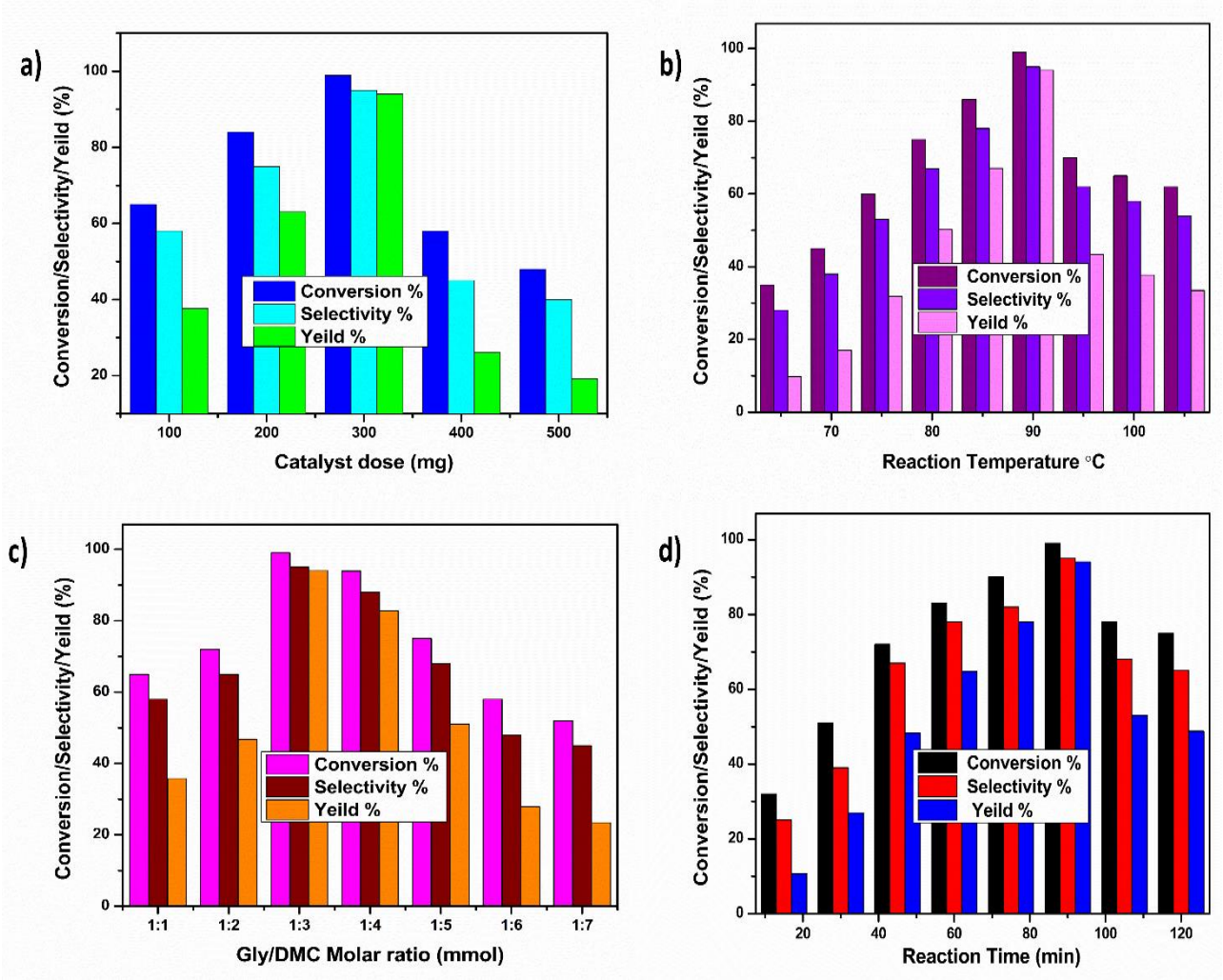


Figure 5.10. Effect of reaction parameters **(a)** Catalyst dose (reaction temperature = 90 ^{0}C, reaction time = 2 hrs, Gly:DMC = 1:2) **(b)** Temperature (Gly:DMC = 1:3, catalyst dose = 300 mg, reaction time = 2 hrs) **(c)** Molar ratio (reaction conditions: catalyst dose = 300 mg with respect to glycerol used, reaction temperature = 90 ^{0}C, reaction time = 2 hrs), **(d)** Reaction time (Gly:DMC = 1:2, catalyst dose = 300 mg, reaction temperature = 90 ^{0}C).

5.7. Green metric studies

The increasing environmental awareness has started giving more prominence to waste prevention and remediation. For this prospect, green chemistry comes to play its role that focuses on properly utilizing each substrate, carbon-neutral processes, solvent-free processes, and elimination of toxic wastes. Different green metric parameters for evaluation of the environmental effect on synthesis procedures are E – factor, PMI (process mass intensity), CE (carbon efficiency) expressed as

$$\textbf{E – factor} = \frac{\textbf{mass of the waste (g)}}{\textbf{Mass of desired product(g)}} \quad \textbf{(5.1)}$$

$$\textbf{PMI} = \frac{\textbf{Total mass used in process(g)}}{\textbf{Mass of final product(g)}} \quad \textbf{(5.2)}$$

$$\textbf{CE\%} = \frac{\textbf{No of moles of GLC} \times \textbf{No of carbon in GlyC} \times 100}{\textbf{Moles of glycerol} * \textbf{No of carbon in glycerol} + \textbf{No of moles of DMC} \times \textbf{No of carbon in DMC}} \quad \textbf{(5.3)}$$

The E –factor value was calculated by considering the substrates, reagents, products, and catalysts. All through the transesterification reaction of glycerol, methanol produced as a by-product, was not considered waste because it was recovered and further used in biodiesel production. Thus, the estimated value of the E – factor comes out to be 0.83, which lies in the range of 0 to 1, confirming that the catalyst is environmentally compatible. Process mass intensity deals with the sustainability of the organic synthetic procedures in chemical reactions. This includes the efficiency of the followed reaction procedure, amount of solvent, reagents, and stoichiometry in synthesis procedures. Mathematically, PMI can be expressed in equation. 6 whose ideal value should be 1 i.e., total mass used in the process should be equal to the mass of the obtained final product. In this process, PMI is estimated to be 1.54 g^{-1}, which shows the greenness of the process followed. Further, carbon efficiency for the transesterification of glycerol was estimated to be 0.54, which comes in the range of 0 to 1, which signifies the synthetic procedure's greener nature. Thus, transesterification of glycerol follows an

environment-friendly synthetic procedure, and the entire process is environmentally compatible [164, 165].

5.8. Recyclability study

The endurance capacity of the NDW catalyst was checked by performing a recyclability study illustrated below as Figure 5.11. The reusability of the synthesized NDW catalyst was studied under augmented reaction conditions, viz. glycerol – 1 mmol, DMC - 3 mmol, catalyst – 300 mg, reaction temperature – 90 ℃, agitation speed – 620 rpm. After the reaction, the catalyst was separated by filtration and then washed with CH_3OH 3-4 times to remove the impurities and organic matter adsorbed on the catalyst's surface. Afterward, the recovered catalyst was oven-dried at 110 ℃ and regenerated by calcining at 900 ℃ (Table 5.1) [142]. The regenerated catalyst was undergone for further batch experiments up to 5 reaction cycles, and the activity was checked by evaluating the conversion of glycerol. In order to validate the stability of the reused catalyst, XRD studies were performed. It was found that the crystallinity of the NDW after recyclability remains intact, which is the reason behind the high conversion obtained through recycled catalyst. It was found that conversion slightly decreases to 80 % after the fourth reaction cycle, and after the fifth cycle, the conversion decreases to 73 % due to a slight loss in the active sites. Only some of the active sites get leached confirmed by performing a leaching test done by performing a hot filtration test. During the experiment, 0.46 gm of NDW catalyst was poured into 24.5 mL of DMC and taken in a conical flask with conventional heating at 90 ℃ for 90 min at constant agitation. After the reaction, the catalyst was segregated, glycerol 15 mL was added to the remaining filtrate, and applied the same reaction condition. After the reaction conversion of glycerol was checked and compared with the catalyzed experiments. The following equation determined leaching % as below:

$$\textbf{Leaching \%} = \left(1 - \frac{\textbf{weight of the reused NDW catalyst}}{\textbf{weight of fresh NDW catalyst}}\right) \times 100 \qquad (5.4)$$

It was observed that the raw DW (distillation waste) suffered severe leaching of about 25.2 %, which is overcome by incorporation with Ni metal to form NDW catalyst. The synthesized NDW catalyst suffered a slight leaching of around 6.7 % due to the loss of active metal sites. Thus, the NDW catalyst was stable up to 5 reaction cycles and gave appreciable conversion towards the formation of glycerol carbonate.

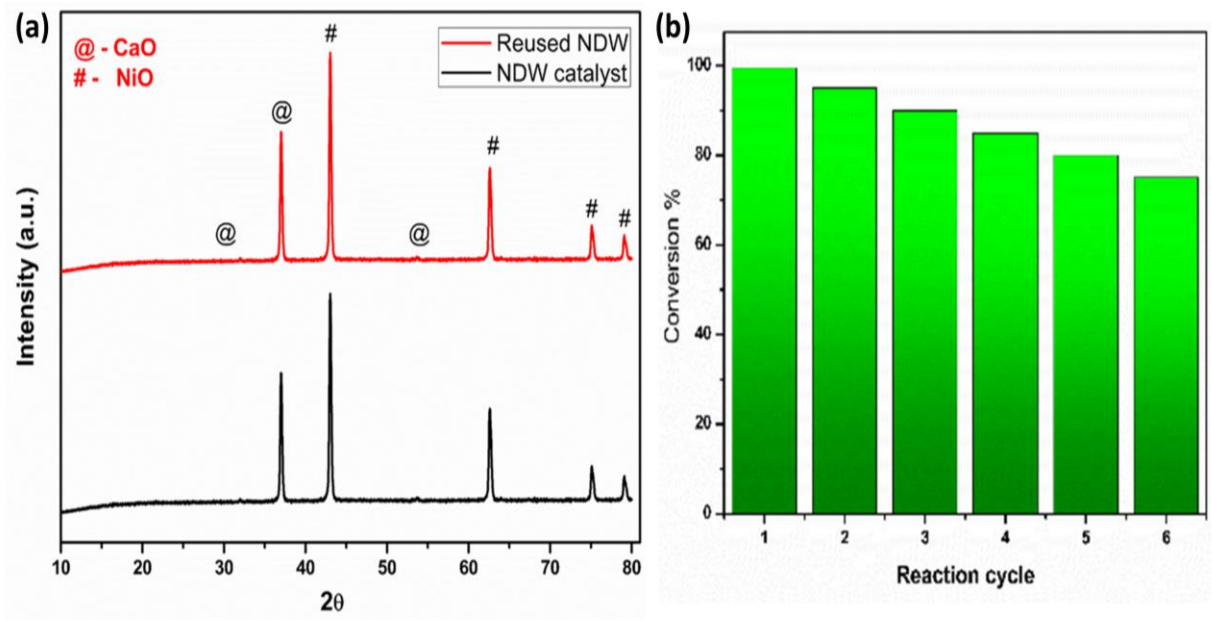


Figure 5.11.(a). XRD diagram of reused NDW catalyst, **(b).** Reusuability of the synthesized NDW catalyst.

Table 5.1: Effect of pretreatment on reusability of the catalyst

Catalyst Condition	**Fresh catalyst 1st cycle conversion (%)**	**Reused 2nd cycle conversion (%)**	**Reused 6th cycle conversion (%)**	**Regeneration technique**
Before pre-treatment	78	60	12	Thermal pre-treatment by calcination
After pre-treatment (Calcination at 900 ℃)	99	96	75	Thermal pre-treatment by calcination

5.9. Comparison study

The comparison study of the NDW catalyst with the pioneer results for the transesterification of glycerol is presented in Table 5.2. The catalyst 3CaLa reported by Kumar et al. showed a lower yield of 74% at moderate reaction conditions but came with a higher ratio of glycerol and DMC, i.e., 1:5 [166]. In contrast, NDW utilizes lower glycerol to DMC molar ratio of 1:3 to achieve a higher glycerol carbonate yield of 94%. Likewise, Mohanty et al. reported RK30%-800 catalyst, which shows a good yield of 93.27% but conversion decreases after the fourth reaction cycle [124] whereas NDW shows good catalytic activity till the fifth reaction cycle. Wang et al. reported a DBDWS catalyst, which presents an appreciable glycerol carbonate yield but uses higher glycerol to DMC concentrations in the reaction mixture [167]; Song et al. reported good catalytic activity of Li/ZnO catalyst. However, catalyst takes a long reaction time [168]. Likewise, an egg shell based catalyst takes longer time to get the appreciable conversion. [169]. These comparisons depict that the synthesized distillation waste-based catalyst i.e., NDW is a cost-effective catalyst and showed catalytic activity at moderate reaction conditions.

Table 5.2. Comparison study of synthesised NDW catalyst with the previous reports.

Catalyst/ References	**Optimized reaction conditions Temp (°C)/ Time (h)/ Molar ratio (mmol)/ Catalyst dose (wt.%)/ Basicity (mmol/g)**	**Glycerol conversion/ Selectivity towards glycerol carbonate (%)**
DBDWS [167]	75/2/1:5/2/15.5	95.6/97.9
Oil palm fish ash [170]	80/1.87/1:5/5/12.6	97.3/97.9
Cu/Mg-Al (MAC-0.6) [171]	90/1.5/1:5/3/0.98	96.4/94.6
Red Mud [172]	75/1.5/1:3/12.5/32.1	96.8/96.3
10% NaOH doped ladle furnace [173]	75/1.5/1:2/3/0.14	99/97.9
Calcined dolomite [174]	75/1.5/1:3/6/-	97/96.9
CaO from egg shell [169]	60/3/1:2.5/0.08/0.48	96/97.9
NDW (Present Work)	90/1.5/1:3/3/35.65	99.2/94.9

6. Conclusion

Distillation waste-based nickel modified catalyst was synthesized by a simple wetness impregnation method via a reaction between raw distillation waste and nickel nitrate at different reaction temperatures. The catalytic efficiency of the synthesized catalyst was investigated for the transesterification of glycerol to GlyC using DMC and glycerol as reactants. The results establish that in contrast to other synthesis methods like coprecipitation and hydrothermal catalyst synthesis, the wetness impregnation method shows noticeable results for the glycerol conversion. The physicochemical properties like TGA reveal that the catalyst is stable at 900 ℃ and above and shows the crystalline behavior ascertained from XRD. The catalyst is of the varying spheroidal shape of two types of crystals of CaO and NiO, whose average particle size is 25.68 nm. Basicity of the catalyst reveals that the catalyst is moderate basic, and consists of 35.65 mmol/g of basic sites, that facilitates the deprotonation of glycerol. The reaction parameters were also augmented, and it was found that glycerol to DMC molar ratio, which is 1:3, catalyst amount, which is 300 mg, reaction time 90 mins, and reaction temperature of 90 ℃ are responsible for achieving higher conversion of glycerol of 99.2 % and higher selectivity of 95 % with 94.02 % yield towards glycerol carbonate. Additionally, TOF of the synthesized NDW is 9.74 h^{-1} signifies the good efficiency of the catalyst towards transesterification reaction. To show the environment compatibility of the process followed, green metric parameters are determined, which shows that the synthesis of NDW catalyst and glycerol carbonate follows a greener route. Our results show that distillation waste is an ideal source for making Ni-Ca-O mixed metal oxide catalyst since it decreases the overall cost of the catalyst and, as a result, lowers processing costs. We believe that this information is crucial for developing a highly efficient distillation waste-based heterogeneous catalyst that is cost-effective and environmentally friendly for the manufacture of GlyC on an industrial scale.