Chapter 4

Synthesis of Na/TiO$_2$ catalyst for synthesis of biodiesel derived glycerol to glycerol carbonate: Optimization and green metrics studies

4.1. Introduction

The present study reports the synthesis of a binary functional Na- Ti acid-base catalyst for the transformation of bioglycerol to glycerol carbonate. Being non -toxic, having good basic strength and shows high catalytic activity, Na is chosen as an active metal center which facilates the deprotonation of bioglycerol. Ti being known for its thermal and chemical stability, resistant to poisoning of surface-active sites, thus supports acid- base centers present on catalyst. In the synthesized catalyst, Ti provides the Lewis acid centers for the facile transesterification of glycerol and DMC molecules. Few studies have been found on the activity of Na as an active metal for the conversion of glycerol-to-glycerol carbonate. Incorporating sodium nitrate on TiO_2 support, which is thermally and chemically stable, facilitates its role as a stable heterogeneous catalyst. This study focused on the activity of incorporation of Na metal as an active metal on titanium isopropoxide following wetness – impregnation synthesis procedure. To study the physical and chemical property of the fabricated catalyst, detailed characterization including XRD, TG-DSC, FTIR, XPS and TEM analysis were explored. The catalytic activity of the fabricated catalyst has been checked by performing transesterification reaction. E-factor study also explored to ascertain the greenness of the reaction. To the best of our knowledge, this is the first report which explores the catalytic activity of sodium hexatitanate in the transformation of bio glycerol to glycerol carbonate. Easily available and versatile acceptable spectroscopic techniques (^{1}H and ^{13}C NMR) were utilized to study the conversion of the glycerol-to-glycerol carbonate.

4.2 Experimental

4.2.1. Synthesis of the Na/TiO₂ catalyst

The Na promoted TiO_2 based catalysts were prepared by wetness incipient method as well as precipitation method at room temperature. All the precursor chemicals were procured from Sigma Aldrich, India, and were used without additional purification. During the preparation of

catalyst through wetness incipient method, sodium titanate was prepared by pouring sodium nitrate solution into titanium isopropoxide solution. Firstly, the saturated solution of sodium nitrate was prepared, taking the required amount of $NaNO_3$ and dissolve in double distilled water, followed by impregnating the powder titanium isopropoxide by saturated $NaNO_3$ solution. The resultant mixture was kept under constant stirring at 80 °C for 1 hour, followed by stirring at room temperature for 8 hours to attain maximum dispersion of ions into the precursor molecules. After that, the mixture was heated at 80 °C at the constant stirring of 500 rpm to evaporate excess water and convert it into xerogel, i.e., slurry-like material. The xerogel was kept for drying in a hot air oven at 120 °C overnight. The dried sample was undergone for thermal heat treatment in an air muffle furnace at different temperatures 400 °C, 700 °C, 900 °C for 5 hours named as 400TNO, 700TNO, and 900TNO respectively [130]. After attaining the stable pretreatment temperature, the catalyst with varying Na content is synthesized and named 5TNO, 10TNO, and 20TNO. During coprecipitation synthesis of Na promoted titanium oxide, the required amount of sodium nitrate solution is added into an appropriate amount of titanium isopropoxide solution. The resultant mixture is stirred for the complete dissolution of constituent metal salts. After that, ammonium hydroxide solution is added drop-by-drop till complete precipitation of metal nitrates to hydroxides. The gel is kept for stirring overnight for the aging of the precipitated mixture. Further, the precipitate is filtered out and dried on its own for 8 hours and calcined to obtain the catalyst. The preliminary confirmation of stability of the catalyst and its phase has been checked through TGA and XRD analysis, respectively. The thermally activated catalysts undergone for transesterification to check their catalytic activity, and the physicochemical property of the catalyst synthesized was studied through performing several characterization techniques as described below. The schematic diagram of synthesis of catalyst is depicted in Figure 4.1.
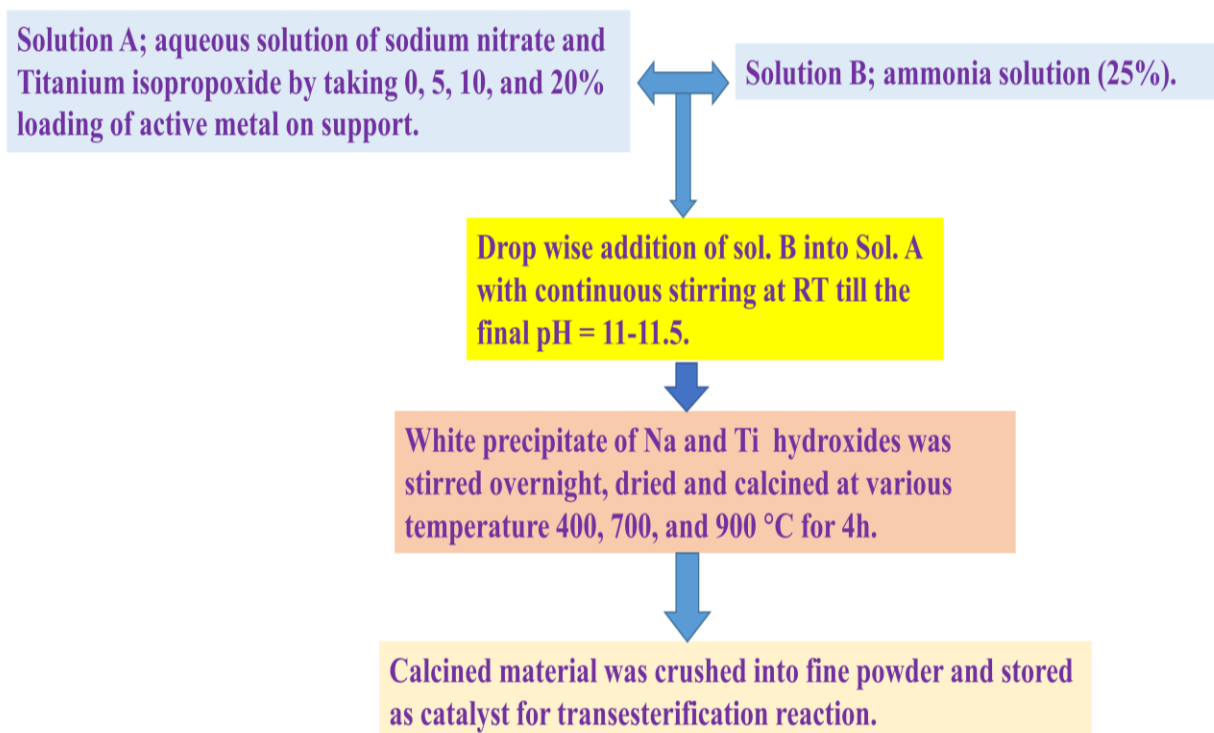
Figure 4.1: Synthesis of Na/TiO_2 catalyst.

## 4.3 Characterization of the catalyst

To study the physicochemical properties, the catalyst prepared was underwent for several characterizations.

4.3.1. Thermogravimetric analysis of the synthesized catalyst

To investigate the thermal characteristics of synthesized 10TNO catalyst, the uncalcined catalyst was undergone for TGA-DSC analysis to study the weight loss and heat flow against the temperature. From Figure 4.2, it can be visualized that the total mass loss of 19.53% occurred via the following processes. Firstly, the mass loss of around 100 °C corresponds to a broad endothermic peak due to removing surface physiosorbed water molecules. An endothermic peak at 303.87 °C with a heat flow of 34.6296 J/g is due to the loss of crystallization water. Further, small exothermic peaks show the removal of organic moieties present in the catalyst at around 480 – 580 °C. The significant mass loss can be seen above 600 °C to 680 °C (of 19.306%) attributed to the formation of $Na_2Ti_3O_{16}$ from its respective nitrates

and hydroxide precursor via thermal decomposition. After that, no further mass loss was observed, anticipated that the catalyst is stable at 700 °C and above temperatures [131].
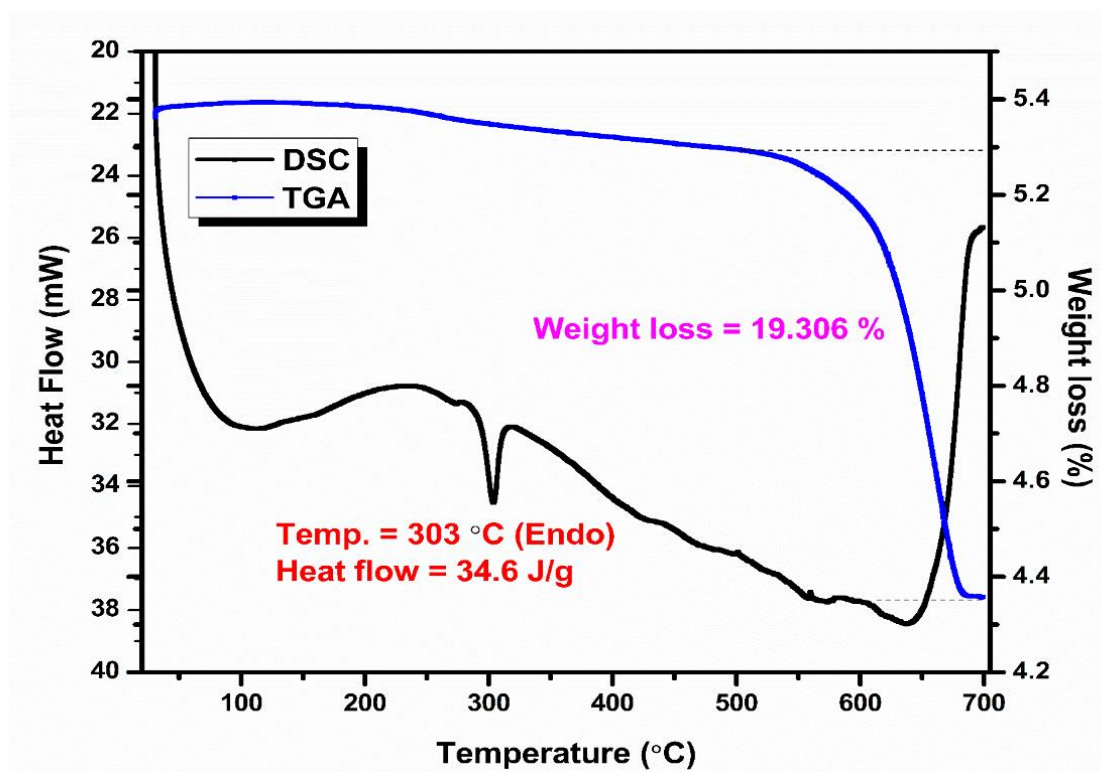
Figure 4.2 TGA – DSC plot of 10TNO (without calcination).

4.3.2. X-ray diffraction studies

The X-ray diffractogram of TiO_2 & Na modified TiO_2 catalyst with varying sodium concentration (0-20 wt.%) calcined at 900 °C is represented in Figure 4.3a. The diffraction peaks originated at 2θ 25.15 corresponds with miller indices (101), 36.63 with (004), 37.38 with (200), 38.31 with (105), 47.78 with (211), 54.75 with (204), respectively corresponds to the anatase phase of TiO_2. Some minor peaks are also included, corresponds to the rutile phase showing diffraction peaks at 68.36º with miller indices (220), 74.95º with (215) miller index. On increasing Na concentration, new diffraction peaks have appeared, forming Na-Ti mixed metal oxide having composition, i.e., $Na_{2-y}H_yTi_3O_7$ (0≤y≤2). At lower Na concentration, a mixed-phase of $Na_2Ti_6O_{13}$ and TiO_2 appeared. The increasing Na concentration to 10 wt.(weight)% on TiO_2 support leads to the formation of pure sodium hexatitanate i.e. $Na_2Ti_6O_{13}$

crystal matched with JCPDS File no. 01-072-1398. The crystal system is monoclinic consisting of C 2/m space group and crystal structure paramter are cell parameters a = 15.12, b = 3.738, c = 9.16 A^0; $\alpha = \gamma = 90^0$, $\beta = 99.3^0$. Further, increasing the concentration of Na transforms the sodium hexatitanate to sodium trititanate crystal i.e., $Na_2Ti_3O_7$, consistent with JCPDS file no. 31-1329. This structure evolution from $Na_2Ti_6O_{13}$ to $Na_2Ti_3O_7$ sodium titanate is achieved by rearrangement and sharing of one coordinated O atom resulting in the formation of Na - Ti ion located 3-D compact microporous structure. The crystallite size based on the highest intensified (200) diffraction peak located at $2\theta = 11.84^0$ calculated through Scherrer formula is coming out to be 37.3 nm.

$$d = \frac{0.9\lambda}{\beta\cos\theta} \qquad (4.1)$$

The Influence of pretreatment temperature on the crystal arrangement was also explored. Figure 4.3b depicts the XRD diffractogram of 10TNO calcined at 400 °C, 700 °C, 900 °C. It was observed that at temperature 400 °C, the sodium ions arrange to form the trititanate structure, i.e., $Na_2Ti_3O_7$ with lower crystallinity, validates by JCPDS database file no. 01-072-0148. An increase in temperature to 700 °C changes the sodium trititanate structure to hexatitanate but with lower crystallinity and impure phase i.e., along with peaks of $Na_2Ti_6O_{17}$, extra peaks are observed, showing the existence of some minor phase as well. This endorsed the alteration in the crystal structure with dropping crystallinity because of the interaction between metals. Further, raising the temperature to 900 °C results in the formation of pure sodium hexatitante i.e., $Na_2Ti_6O_{17}$. Therefore, the pretreatment temperature shows a significant role in governing the stability and purity of the crystalline phase formed. Also, 10TNO calcined at 900 °C shows better glycerol conversion because of the stability of the active catalyst, and microporosity, 10TNO calcined at 900 °C is taken as the best catalyst for the conversion of glycerol-to-glycerol carbonate [132, 133].

Further, the catalyst synthesized through coprecipitation shows the diffraction peaks correspond to the TiO₂ anatase phase indicates that during coprecipitation synthesis, sodium precursor acts as a coprecipitating agent instead of the active metal. This results in the formation of the anatase phase. Therefore, the coprecipitation process cannot be achieved for sodium-promoted catalysts.
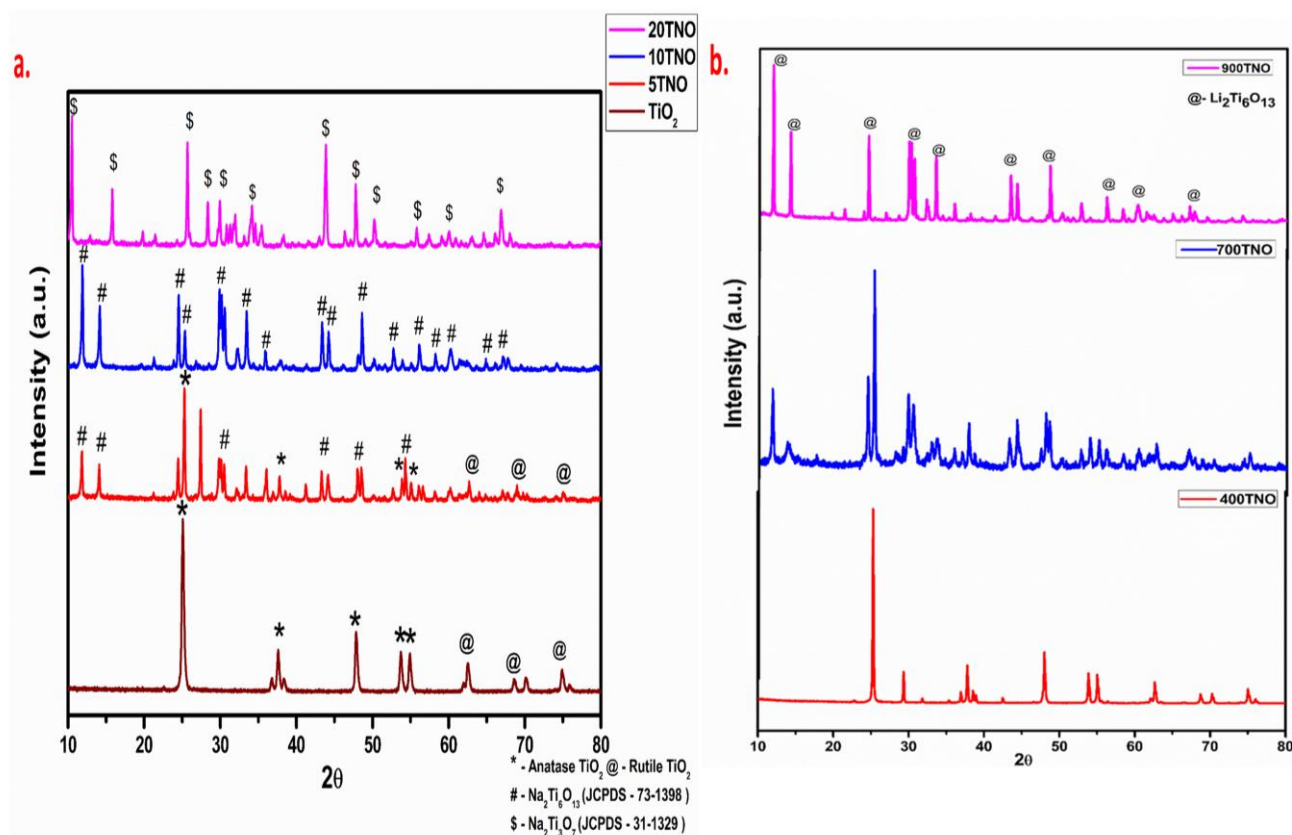
Figure 4.3: XRD patterns of (a) catalyst with varying Na concentration from 0 to 20 wt.% i.e., TiO₂, 5TNO, 10TNO, 20TNO (b) calcination temperature optimization of 10TNO.

4.3.3. XPS Analysis

The oxidation states and the atomic energy level of the different elements present in synthesized catalyst TNO are investigated through XPS analysis depicted in Figure. 4.4. The XPS characteristics peaks were calibrated considering the adventitious C1s peak as the reference showing binding energy at 284.68 eV. In Figure 4.4, the spectra show the existence of Na, Ti, and O in the prepared catalyst. In the sodium spectrum, the characteristics peak appear at 1069.74 eV shows the existence of Na metal present in 1s shell having +1 oxidation

state. The Ti spectrum shows Ti 2p peak seems at binding energies 458.5 eV resembles Ti 2p$_{3/2}$, 464 eV corresponds to Ti 2p$_{1/2}$ with a doublet splitting of 5.7 eV because of spin-orbit coupling of Ti 2p shows the presence of Ti in +4 oxidation state [134]. The peak appears at 471.57 eV shows the satellite peaks having an energy of 5.7 eV. It gives information about strong overlapping between Na 1s and Ti LMM auger peak (840.1 eV). In the O1s spectrum, the characteristic peak at 529.63 eV is due to Na-O and Ti-O metal-oxygen bonding. Additionally, the peak at 535.22 eV suggests the potential overlap of auger peak of Na1s with O1s [135]. The outcomes agree with the Thermo Fisher XPS database and NIST XPS database. The oxidation states of the existing elements display confirmation with the XRD results.
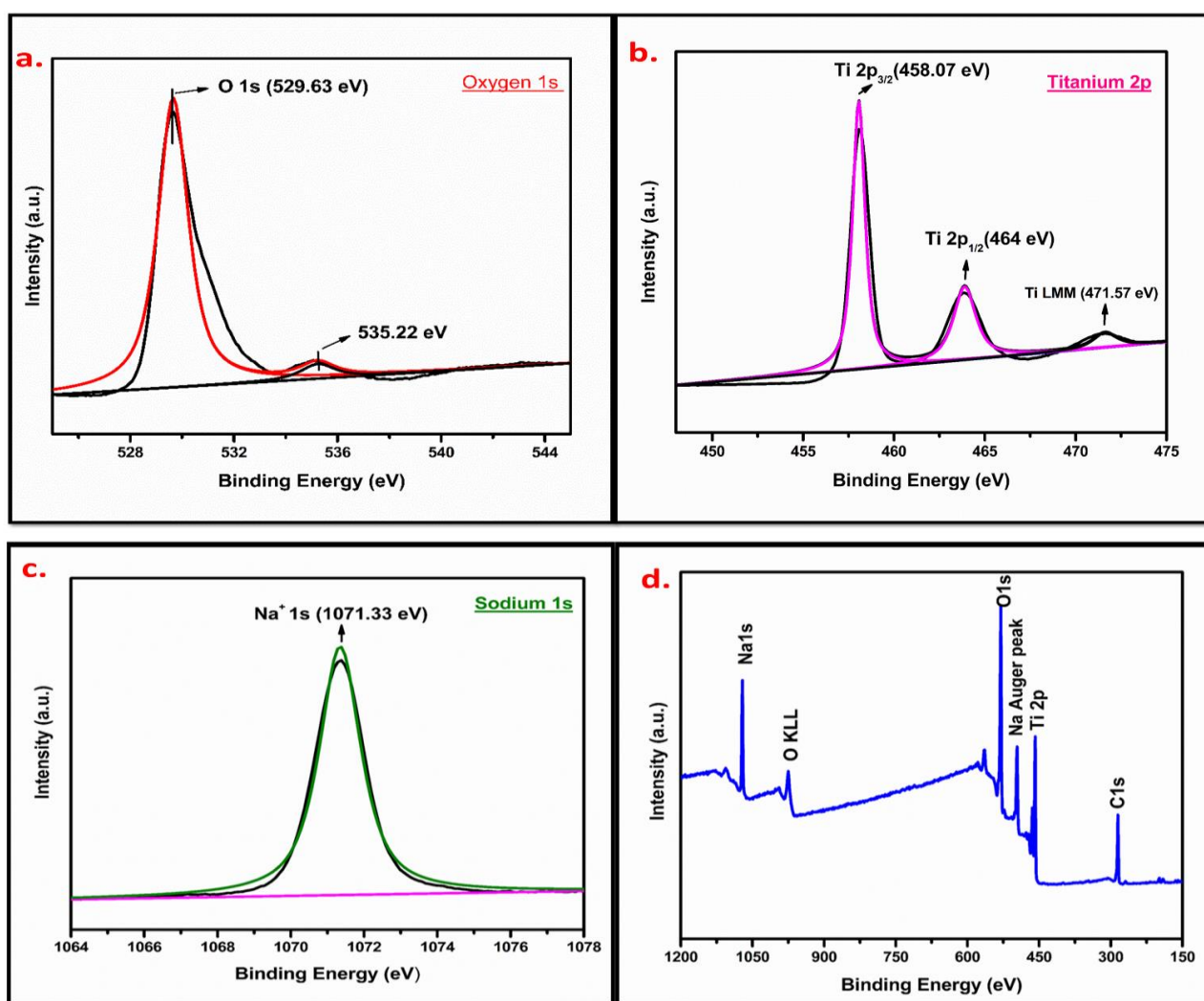

Figure 4.4 XPS plots of sythesized 10TNO .

4.3.4. FTIR studies

FT-IR analysis shows that the functional groups are existing on the catalytic surface play a crucial role in the transesterification of glycerol. Figure 4.5 represents the FT-IR spectra of calcined Na/TiO_2 catalyst with different Na concentrations such as 5TNO, 10TNO, 20TNO, respectively. The broad band appears around 3377 cm^{-1} showing in spectra of each catalyst indicating the O-H stretching vibrations due to moisture chemisorption and Ti-OH moieties' coordination [136]. The small intensity vibrations at 1644.75 cm^{-1} are interpreted as O-H bending vibrations which show shifting from 1637 to 1644 cm^{-1} with increasing Na metal concentration. The high-intensity vibration band at 522.73 cm^{-1} and 710.43 cm^{-1} indicates the oxygen–metal sublattice vibrations of Na-O and Ti – O, respectively. The sharp vibration band aroused at 770 cm^{-1} interpreted the formation of mixed metal oxide (Na-Ti-O bond) [137].
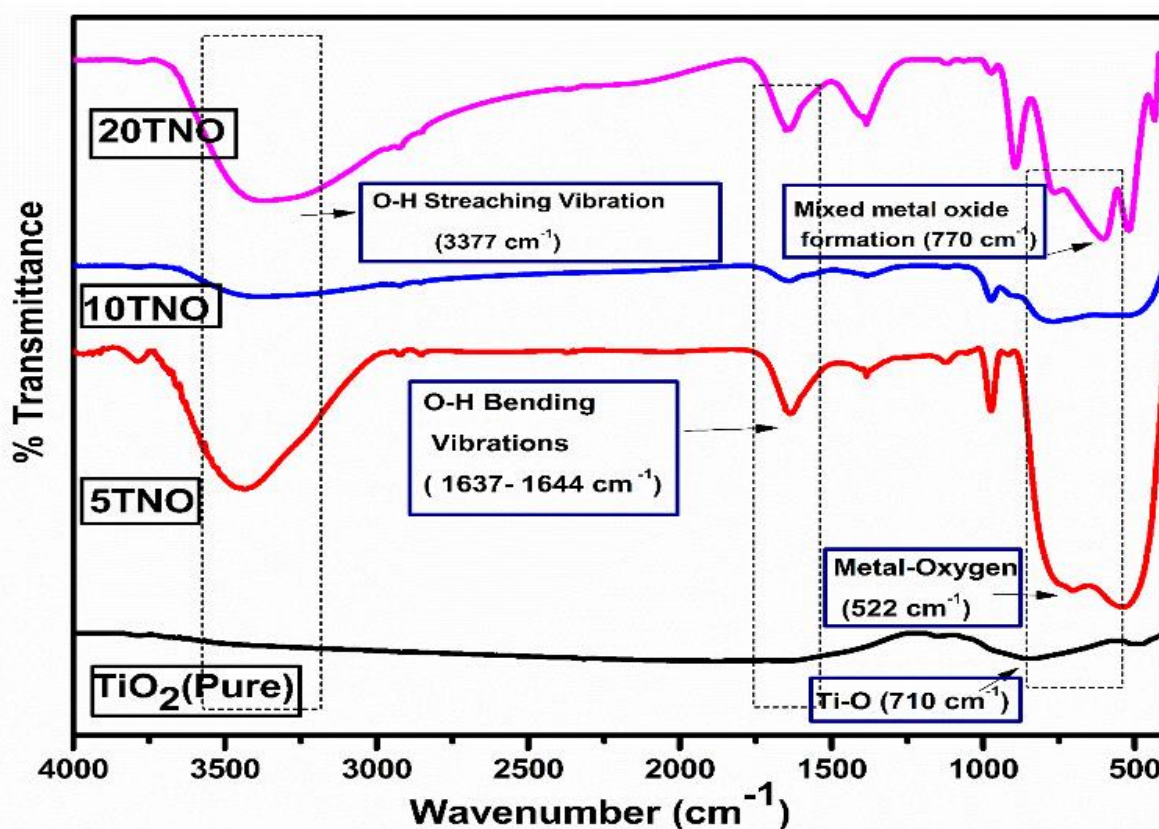

Figure 4.5. FT-IR spectra of TiO_2, 5TNO, 10TNO, 20TNO.

4.3.5. TEM analysis

The microscopic images of synthesized catalysts were studied through TEM spectroscopic analysis shown in Figure. 4.6. The TEM micrograph of the synthesized Na promoted TiO_2 shows rod and spheroid-like morphology (Figure 4.6(a)) entangled with each other as consistent with the literature [138]. The synthesized catalyst was found to comprise particles of irregular sizes. This is because of the agglomeration of the different crystallites to form bigger size particles resulting in the formation of spheroidal shape-like particles. Uniform dispersion of the particles on the crystal structure was also observed. The average particle size is also calculated through micrographs which come out to be 50.24 nm represented through histogram (Figure. 4.6(d)). Moreover, the lattice fringes of 10TNO are aligned in a parallel fashion with inter planer d spacing equal to 0.417 nm correlating to (-2 0 2) plane of $Na_2Ti_6O_{13}$ phase shown in Figure 4.6(b). The SAED pattern shown in Figure. 4.6(c) of 10 TNO confirms the presence of crystalline monoclinic crystal system consisting of planes (6 0 1), (10 0 4), (2 2 6) corresponding to $Na_2Ti_6O_{13}$ phase-matched with JCPDS file 01-073-1398. The result showing the layered structure of 10 TNO agrees well with XRD results. The elemental composition was also determined through elemental mapping by performing energy-dispersive X-ray spectroscopy (EDX), which depicts the uniform distribution of three elements Na, Ti, and O.
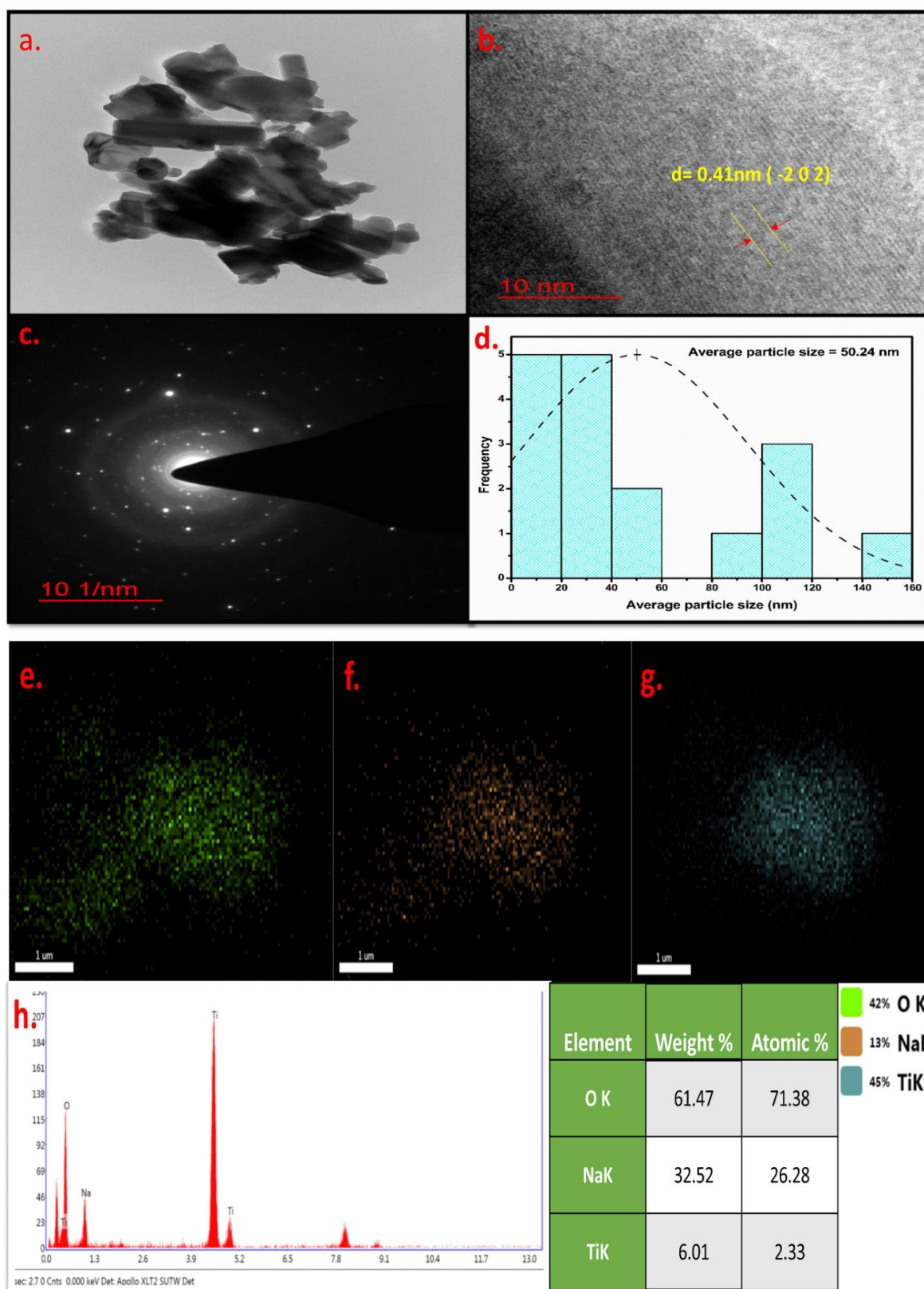
Figure 4.6. TEM micrographs of 10TNO (a) morphology, (b) HR image showing lattice planes corresponding to 10TNO (c) SAED pattern of 10TNO (d) Histogram showing average partice size and (e) elemental mapping of O, (f) elemental mapping of Na, (g) elemental mapping of Ti and, (h) EDX spectra of the synthesized 10TNO

4.3.6. Basicity

The basic strength plays an important role in the transesterification reaction of glycerol with DMC to produce glycerol carbonate. Therefore, the determination of basic strength and basicity of the synthesized catalyst is highly needed. The basic strength and basicity were determined employing Hammet indicator titration using different indicators such as bromothymol blue (H_- =7.2), Phenolphthalein ($H_- = 9.3$), 2,4- di nitro aniline ($H_- = 15.0$), 4- nitro aniline ($H_- = 18.4$) and aniline ($H_- = 27.0$) [139]. During this acid–base titration, 100 mg of synthesized catalyst was added to 10 mL HCl solution having a concentration 0.5 molL^{-1}. The reaction mixture was kept for stirring for the adsorption process for 24 hours in a shaker. Afterward the solid catalyst was separated by centrifugation. The liquid HCl was consisting of adsorbed catalyst undergone for titration with NaOH solution using the above-mentioned indicators. The endpoints are noted, and the base amount present in the synthesized catalyst was calculated by the equation 4.2 below.

$$\text{Basic amount (mmolgm}^{-1}\text{)} = \frac{\text{Initial moles of HCl} - \text{Final moles of HCl}}{\text{Catalyst amount (gm)}} \tag{4.2}$$

It was observed that the basic strength of 10TNO lies in the range of 15< H_-<18.4, which is a moderate basic site and acts as a strong base. This signifies that the number of basic sites and basic strength both influence the catalytic activity of Na modified TiO_2. As it was earlier studied that the high basic strength of the catalyst facilitates the transesterification of glycerol to form glycerol carbonate but higher basic strength results in glycidol formation [140]. Therefore, the catalyst should have moderate basic strength that falls in the range of 15.0 < H_-< 18.4 and have 30.5 mmol/g amount of basic sites. The synthesized catalyst 10TNO calcined at 900 °C displayed the best catalytic activity towards the production of glycerol carbonate.

4.4. Evaluation of activity of catalyst for production of glycerol carbonate

The transesterification of glycerol can be performed in a three-neck round bottom flask of capacity 100 mL attached to a reflux condenser. In order to sustain the temperature and stirring of the reaction mixture, the system was set in an oil bath located on a magnetic stirrer (Tarson digital spinot). During the experiment, 1 mole of glycerol (9.2 g), 2 moles of DMC (1.80 g), and 0.46 gm (5 wt.% of the catalyst with respect to the weight of glycerol (in g) used in the reaction matrix) of the desired catalyst is charged into the batch reactor system and allowed to stir at 500 rpm vigorously until the temperature reaches to 90 °C for 2 hours. After completing the reaction, the catalyst was separated out from the reaction matrix through centrifugation to obtain the liquid product. The recovered catalyst was washed two to four times with methanol and dried in an oven for additional reutilization of the catalyst in the transesterification reaction. After that, the obtained product is undertaken for the ^{1}H and ^{13}C NMR analysis to confirm the desired product formed.

Table 4.1. Screening of catalyst and effect of calcination temperature for synthesis of glycerol carbonate

Catalyst	Crystallite size (nm)	Conversion (%)	Yield (%)
TiO₂	54.5	4.5	4.2
5TNO	38.8	84.3	80.5
10TNO	37.3	98.5	95.1
20TNO	51.6	80.6	76.9
400TNO	33.0	40.5	37.1
700TNO	36.6	82.3	76.1

Reaction conditions – Gly:DMC = 100 mmol:200 mmol, catalyst dose – 0.46 gm, reaction temperature – 90 °C, time – 2 hours
where, Yield (%) = % of conversion of glycerol × % of selectivity of GlyC; GlyC – glycerol carbonate, GD – glycidol

The validity of the formation of the glycerol carbonate is done through performing NMR spectroscopic analysis and the peak obtained were matched to the characteristic peaks corresponds to the glycerol carbonate. During transesterification reaction, as glycerol starts reacting with DMC leads to appearance of multiple peaks showing the incomplete transesterification of glycerol (Figure. 4.7(a)). Further, as the reaction proceed at optimized condition, complete conversion of glycerol-to-glycerol carbonate takes place depicted in Figure. 4.7 (a). The % glycerol conversion was obtained by formula mentioned in equation 1. In ^{1}H NMR spectra, the multiplet observed at 4.77 to 4.81 ppm is mainly govern the formation of glycerol carbonate and its integration peak area determines the % conversion of glycerol-to-glycerol carbonate (Figure 4.7 (a)). The ^{13}C spectra, the chemical shift appears at 61.11 ppm, 66.38 ppm, 77.55 ppm, 155.74 ppm evident the characteristic peaks of number of carbons present in glycerol carbonate shown in Figure.4.7 (b).
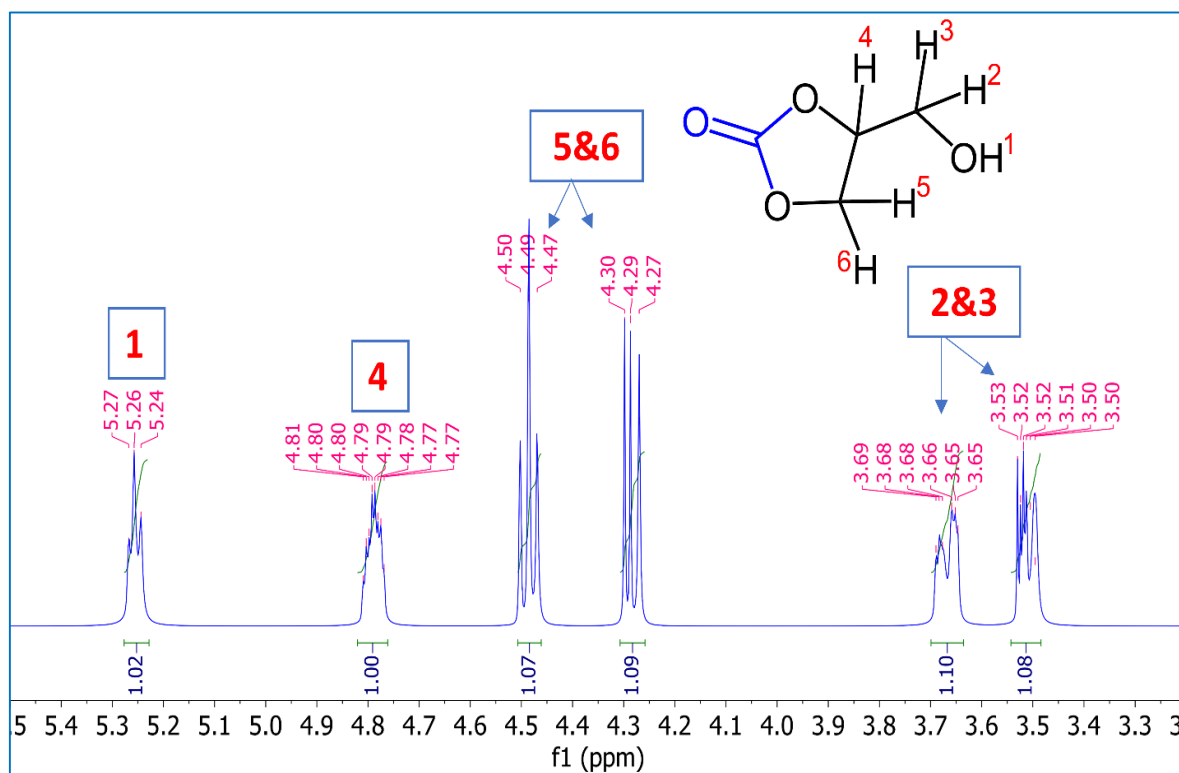
**Figure 4.7 (a)** ^{1}H – NMR of sythesized glycerol carbonate
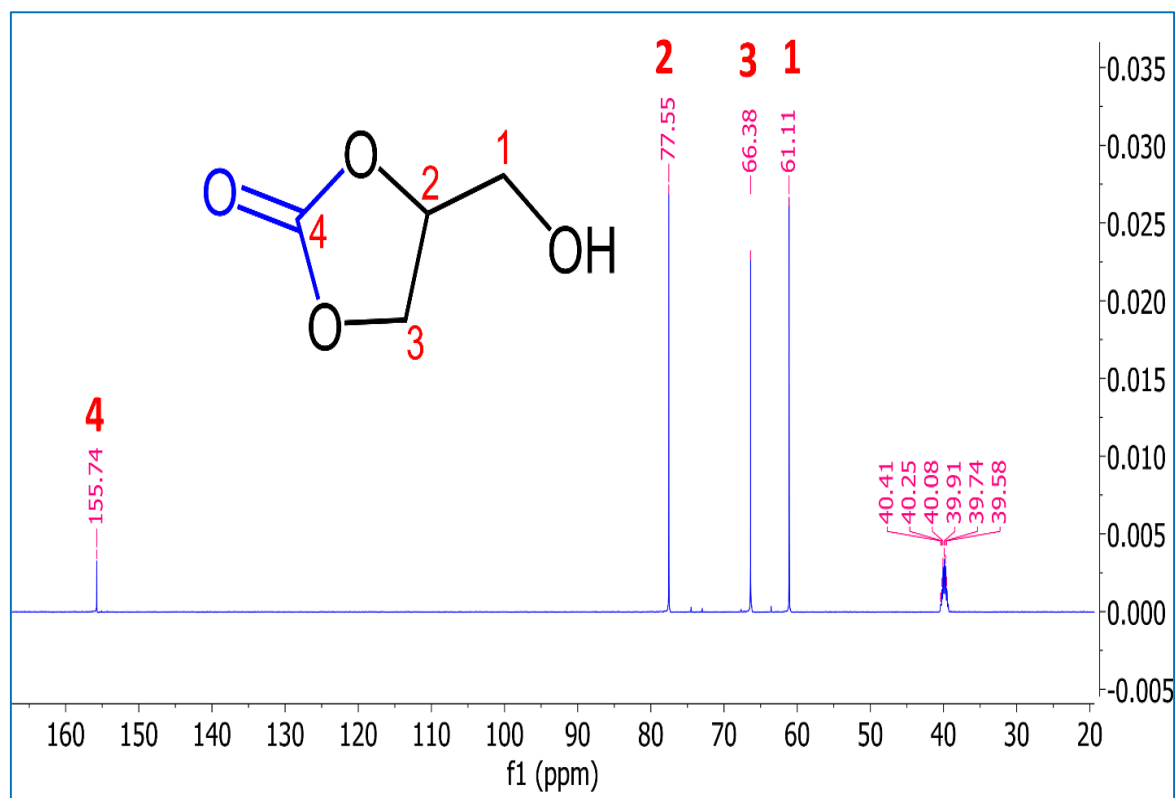
**Figure 4.7 (b)** ^{13}C – NMR of sythesized glycerol carbonate

4.5. Proposed reaction mechanism and characterization of the synthesized product

The reaction of glycerol-to-glycerol carbonate using DMC as a reactant in the presence of heterogeneous catalyst undergoes transesterification reaction depicted in scheme 4.1. A plausible mechanism has been proposed based on the preceding mechanistic studies of the transesterification process of glycerol-to-glycerol carbonate using Na modified TiO$_2$ catalyst presented in scheme 4.2. The transesterification reaction follows the Langmuir-Hinshelwood mechanism (L-H) as reported in previous literature. The active centre of the fabricated catalyst is Na acts as basic centre, and Ti acts as the acidic centre present on the catalytic surface. Following the adsorption mechanism, firstly, the interaction of acidic and basic centre with DMC and glycerol molecules respectively takes place. The interaction of the Na centre increases the nucleophilicity of the glycerol, and Ti centre increases the electrophilicity of the carbonyl carbon of DMC. These interactions facilitate the attack of the deprotonated hydroxyl

group on carbonyl carbon which further undergoes cyclization. This cyclization results in the formation of glycerol carbonate with the elimination of methanol molecules [140].
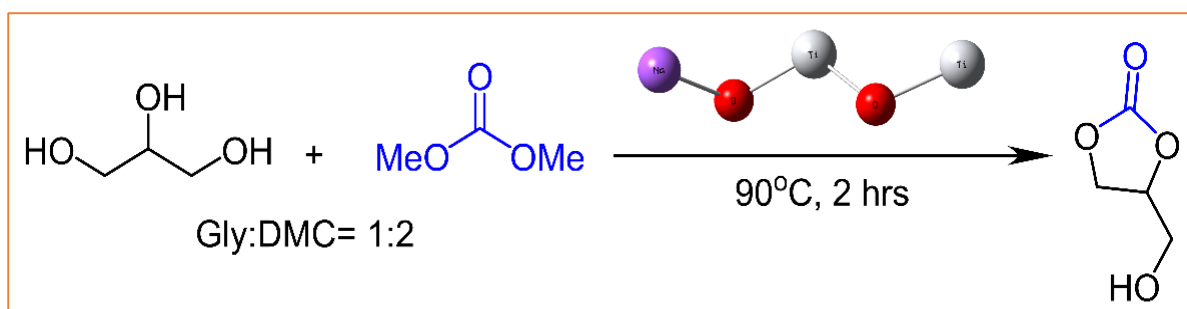
Scheme 4.1. Transesterification reaction of Glycerol with DMC.
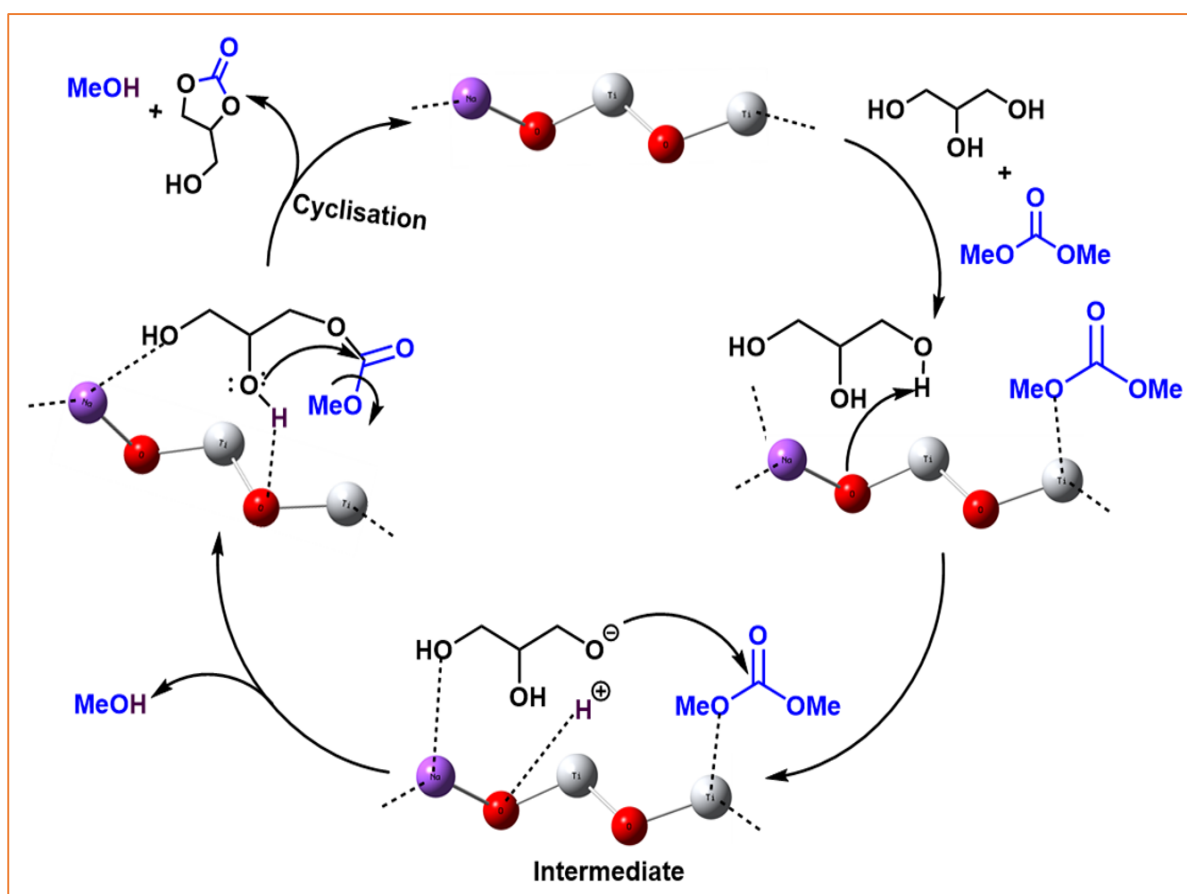
Scheme 4.2. Proposed reaction mechanism for the role of 10TNO during transesterification of glycerol with DMC.

4.6. Optimization of the reaction parameters

4.6.1. Influence of amount of catalyst

The amount of catalyst (w.r.t. weight of glycerol) used in the reaction mixture plays a vital role in the transesterification reaction. Taking all other reaction parameters constant like glycerol to DMC in the ratio of 1:2, time 2 hours, temperature 90 ℃, catalyst dose in the reaction medium is varied, and the conversion was noted. It was observed that the conversion of glycerol rises with increasing catalyst dose from 1 to 3% (from 60 to 98.5% glycerol conversion) and further decreases depicted in Figure. 4.8a. This increase in conversion % is due to the increases in the active basic sites with increasing catalyst amounts. Further, higher catalyst dose in the reaction medium leads to agglomeration of catalyst, which hinders the external mass transfer and blocks the active sites of the catalyst [127].

4.6.2. Influence of molar ratio

The effect of glycerol to DMC molar ratio on glycerol conversion and yield of the product glycerol carbonate was studied by varying the molar ratio from 1:1 to 1:5, keeping all the reaction parameters constant depicted in Figure. 4.8b. It was found that at an equal stoichiometric ratio of Gly to DMC, 55 % glycerol conversion was obtained. With increasing molar ratio to 2, i.e., increasing concentration of DMC increases the conversion to 98.5 % and yield 94.5% as the characteristics polar nature of glycerol makes the molecule adsorb on the catalyst active site. Therefore, more DMC acts as a reactant and solvent, both required for obtaining a high yield. Since transesterification is an equilibrium-based reaction. Thus, an excess amount of DMC is required to shift the reaction towards the forward direction to obtain glycerol carbonate [124].
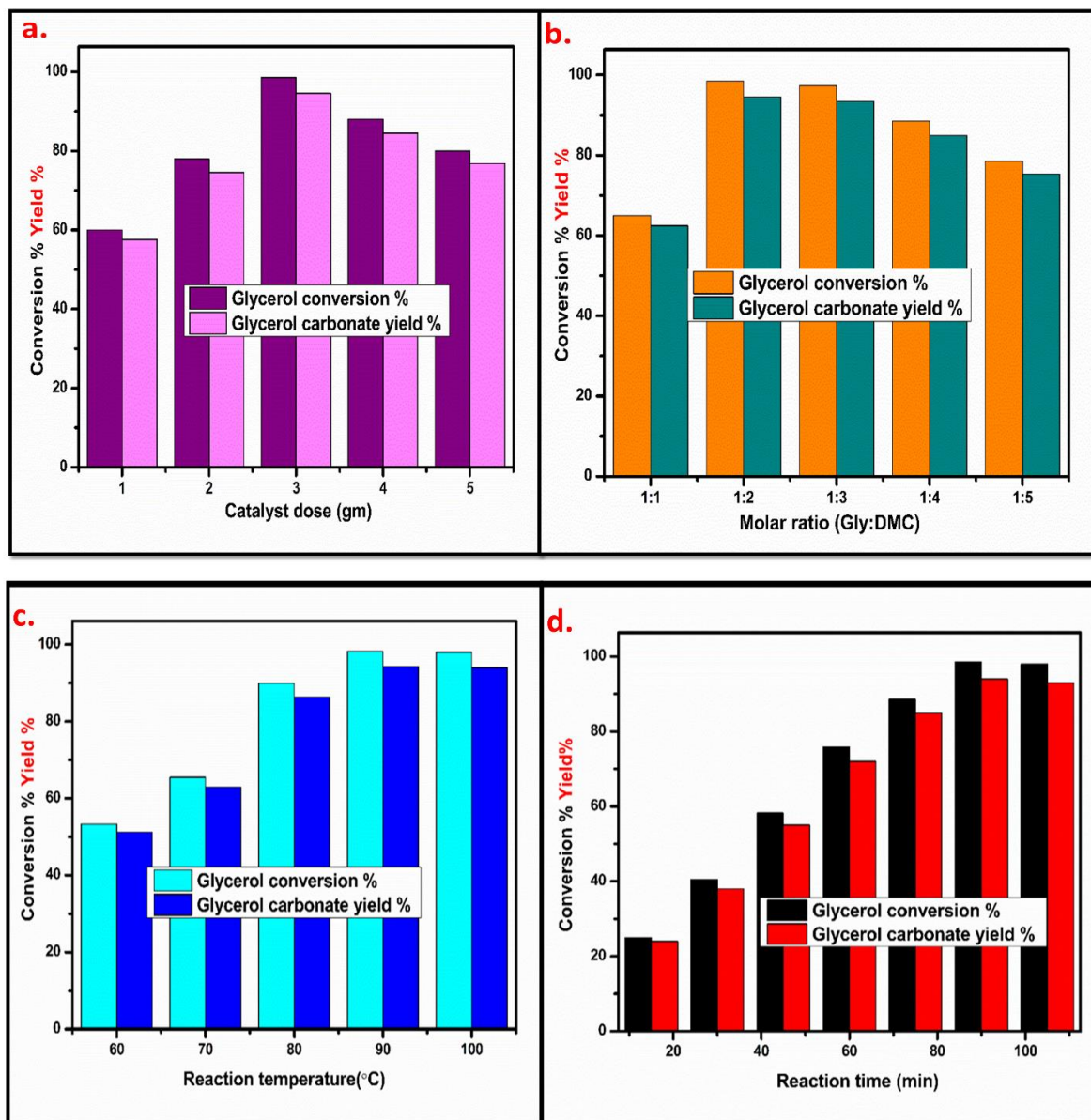
4.6.3. Influence of reaction temperature

Reaction temperature has a significant effect on the efficiency of the transesterification reaction. The temperature has a direct effect on the active sites of the catalyst and on the heat-

sensitive dimethyl carbonate, which considerably governs the reaction efficiency. To study the effect of temperature on glycerol conversion, various experiments were performed, varying reaction temperatures from 60 to 100 °C keeping other parameters constant depicted in Figure. 4.8c. It was found that at a lower temperature from 60 °C to 70 °C, the conversion obtained was very low, i.e., 53.3 % was observed. Further, with increasing temperature to 90 °C, the % conversion also increased from 53.3 to 98.5. This signifies that the higher temperature provides enough energy required to overcome the energy barrier between reactant and product molecules. Further, the increasing temperature would not increase the conversion of glycerol above 90 °C, since the boiling point of DMC is 90 °C and above this temperature, it starts evaporating and making three phasic system in the reaction matrix, one solid phase is the catalyst, the second liquid phase is glycerol, and third gaseous phase is DMC which stops the forward reaction and formation of the product [107].

4.6.4. Influence of reaction time

The effect of reaction time also has a significant effect on the conversion and yield of the product. The effect of reaction time was also explored, keeping other parameters constant as in earlier optimization studies. Experiments were carried out to check the conversion percentage of glycerol at different time intervals. It was found that the conversion % increases with consecutive increases in time, and the lowest conversion obtained was 30% in 20 min and increases to 98.5% in 90 min, illustrated in Figure. 4.8d. On escalating the time, the glycerol conversion remains the same, shows the equilibrium nature of the reaction at that time period, and no further change in conversion after this reaction time was observed [140].

Figure 4.8 Influence of reaction parameters (a) Catalyst dose (reaction temperature = 90^{0}C, reaction time = 2 hrs, GLY:DMC = 1:2) (b) Molar ratio (reaction conditions: catalyst dose = 3 wt% with respect to glycerol used, reaction temperature = 90^{0}C, reaction time = 2 hrs), (c) Temperature (GLY:DMC = 1:2, catalyst dose = 3 wt%, reaction time = 2 hrs) (d) Reaction time (GLY:DMC = 1:2, catalyst dose = 3 wt% reaction temperature = 90 ^{0}C).

4.7. Green metrics study of glycerol transesterification

The impact of glycerol carbonate synthesized from biodiesel by-product glycerol using Na modified TiO_2 catalyst on the environment can be estimated by green parameter studies such as E- factor (environmental factor), atom economy, and Process mass intensity (PMI).

$$\textbf{E} - \textbf{factor} = \frac{\textbf{Produced waste mass (gm)}}{\textbf{Produced glycerol carbonate mass (gm)}} \qquad \textbf{(4.3)}$$

$$\textbf{PMI} = \frac{\textbf{Total mass used in transesterification process (gm)}}{\textbf{Produced glycerol carbonate (gm)}} \qquad \textbf{(4.4)}$$

$$\textbf{Atom economy} = \frac{\textbf{Mass of the product (gm)}}{\textbf{Total mass of all the substance produced (gm)}} \qquad \textbf{(4.5)}$$

$$\textbf{TOF} = \frac{\textbf{m glycerol X glycerol M glycerol}}{\textbf{1000m catalyst t}} \qquad \textbf{(4.6)}$$

The eco-friendly nature of the process adopted and the heterogeneous catalyst used can figure out by these studies. E-factor is the parameter to access the environment compatibility of a chemical process i.e., whether a chemical process is environment friendly or harmful to the environment. Lower value of E-factor indicates the environment benign nature of the process. Mathematically, it is expressed as mass of the waste produced to the mass of the product obtained, whereas PMI is the ratio of total mass used in the reaction matrix to the mass of the product [141] and atom economy can be determined by the ratio of the molecular mass of glycerol carbonate to the molecular mass of reactants. The only by-product produced is methanol which is further utilized in biodiesel production. The reusability of the catalyst and solvent is neglected during the calculation of the above green parameters. A lower value of E-factor and PMI shows that lesser waste is generated during the process. The E-factor, PMI, and atom economy come out to be 0.83, 1.72 g^{-1}, 100%, respectively signifies the lesser waste generated and greenness of the process. Also, the instantaneous efficiency of the catalyst expressed as the turn over frequency of the active catalyst is expressed in terms of TOF and comes out to be 9.72 h^{-1}.

4.8. Endurance competency of Na/TiO$_2$

The endurance of the Na/TiO$_2$ can be tested by checking the stability, potential activity, and recyclability of the catalyst. In order to check the reusability of 10TNO, successive batch reactions of transesterification of glycerol were executed, and found that the synthesized catalyst undergoes reusability up to 5 consecutive runs under the optimized reaction parameters. Subsequently, the catalyst was recovered from the reaction matrix through centrifugation and washed with CH$_3$OH two to four times. The recovered catalyst was dried in an oven at 100 °C and recalcined at 900 °C. The obtained regenerated catalyst undergoes transesterification reaction of glycerol with DMC and conversion was noted. It was observed that the conversion and yield decreased slightly with consecutive runs from 80% and 71%, respectively (Figure. 4.9). Also, the basic strength of the catalyst undergoes fifth reaction cycle reduce from 15< H_<18.4 to 9.3 < H_ < 15, confirmed by the Hammet indicator test. The calcined recycled catalyst gives more GlyC yield than the uncalcined regenerated catalyst.

One of the factors responsible for lessening the glycerol conversion is leaching of Na - basic sites determined by

$$\textbf{\% Leaching} = \left(1 - \frac{\textbf{Weight of reused catalyst}}{\textbf{Weight of fresh catalyst}}\right) \qquad \textbf{(4.7)}$$

The leaching % obtained was 4.65 % at Na active metal sites. Also, the XRD analysis shows that reusability leads to a change of phase of the catalyst, i.e., Na$_2$Ti$_6$O$_{13}$ (JCPDS file no. 014-0277) with the appearance of less sharp peaks due to loss in crystallinity. Further, the crystallinity reverts back on thermal treatment results in the formation of the active phase of the catalyst i.e., Na$_2$Ti$_6$O$_{13}$ (JCPDS file no. 01-073-1398). But, the decreasing crystallinity of the peaks appearing in XRD pattern after reused catalyst leads to a decrease in glycerol conversion (Figure. 4.9) [142]. Though, the good efficiency and high stability of the catalyst up to five consecutive runs commends to the commercialization of 10TNO for commercial purpose.
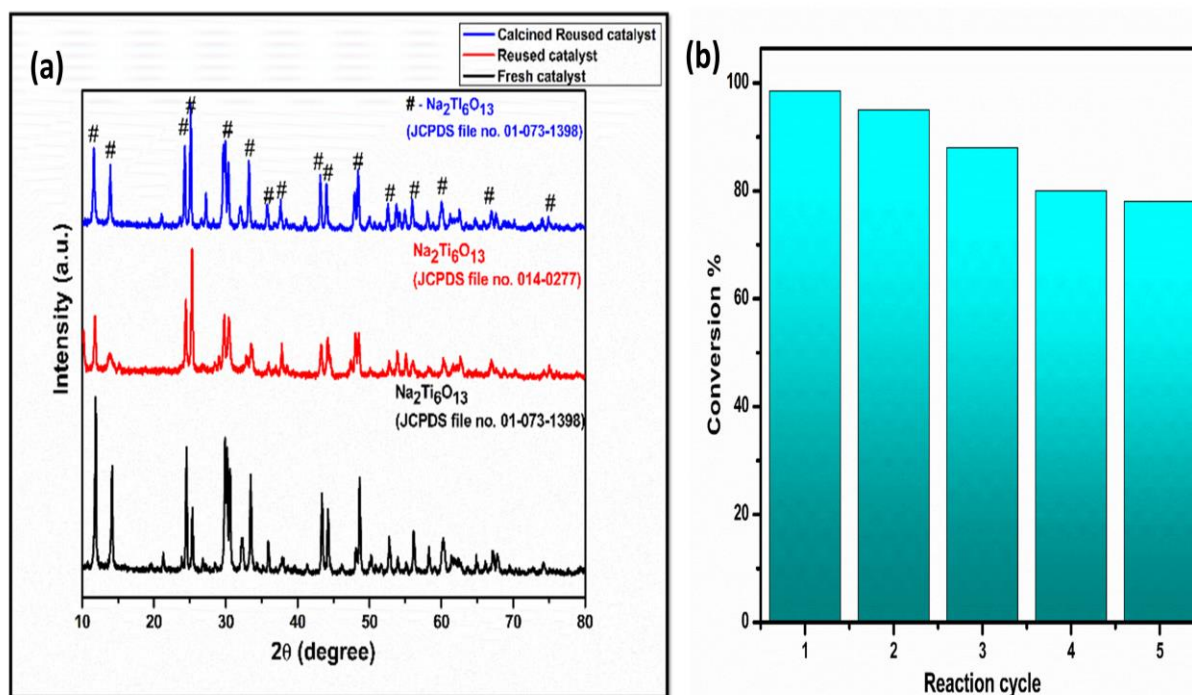
Figure 4.9 (a) Reusuability of the Na/TiO_2, **(b)** XRD diagram of reused catalyst

4.9. Comparison of the synthesized catalyst with the previously reported catalysts

A comparative study of the synthesized 10 TNO catalyst and previously reported catalysts suggests the good activity and efficiency of the catalyst towards glycerol conversion. Most of the previous studies do not include an important catalytic parameter (TOF) [129, 143]. The TOF value is consistent with the values reported in the literature, i.e., catalysts like $MgO-ZrO_2$, MgO consisting TOF value lies in between $0.5 – 16.11 \ h^{-1}$ reported by Parmeswaram et al. [122]. Similarly, Cu-Zn-Al hydrotalcite catalyst has a TOF value in the range of $1.50-5.99 \ h^{-1}$ reported by Kumar et al. [144]. This comparison shows the quite good efficiency of a synthesized 10TNO catalyst with a TOF value of $9.72 \ h^{-1}$. Previously reported catalyst viz. Li-La_2O_3 [145] and 0.3 KF/La –Zr [121] are based on relatively costlier and very less abundant lanthanides. In addition, a catalyst like HTC-Ni requires 1,4 butanediol as a solvent during the reaction [129], KF/Al_2O_3 employed DMF as a solvent for obtaining higher conversion [146]. Ti-SBA takes a larger reaction time for obtaining a better yield [118]. Although $BaCO_3/C$ has

97.9 % conversion, it requires a higher Gly: DMC molar ratio, DMF as a solvent, and lower recyclability [147] than the catalyst reported here. Also, several previous studies do not define the green metric of their synthesized catalyst [148, 149, 150] as in this study. In order to overcome these disparities, a heterogeneous catalyst, i.e., $Na_2Ti_6O_{13}$, was synthesized utilizing nontoxic and low-cost precursors that follows a solvent-less synthesis pathway and are suitable for mild reaction conditions to produce glycerol carbonate.

Table 4.2. Comparison of Catalytic Activity of synthesized $Na_2Ti_6O_{13}$ with various reported heterogeneous catalysts for Gly transesterification with DMC

Catalyst	Reaction time (min)	Reaction temperature (°C)	Gly:DMC molar ratio (mmol)	Solvent	Glycerol Conversion (%)	Endurance capacity	Reference
Ti-SBA-15	240	87.5	1:5	free	94	5th reaction cycle	[118]
Mg/Zr/Sr	90	90	1:5	free	96	4th reaction cycle	[122]
Mg/Al/Zr	90	75	1:5	free	Conversion not reported 94 Yield	Not studied	[151]
Li-La₂O₃	180	85	1:3	free	94.4	3rd reaction cycle	[145]
HTC-Ni	120	100	1:3	1,4-Butanediol	55	4th reaction cycle	[129]
BaCO₃/C	120	140	1:5	DMF	97.9	3rd reaction cycle	[147]
0.3 KF/La -Zr	60	80	1:4	free	91.77	5th reaction cycle	[121]
KF/Al₂O₃	120	75	1:2	DMF	96	3rd reaction cycle	[146]
Mg–La mixed oxide	90	85	1:2	Free	Conversion not reported 83.1 Yield	Poor in 1st cycle itself	[143]
Na₂Ti₆O₁₃	90	90	1:2	free	98.5	5th reaction cycle	Present work

5. Conclusions

In the present study, a heterogeneous catalyst sodium hexatitanate was synthesized via the simple wetness impregnation method. The physicochemical properties of the synthesized catalyst were explored through different characterization techniques, including TGA-DSC, XRD, XPS, FT-IR, TEM, and EDX spectroscopy. The XRD and TGA results revealed the transformation of Na, Ti, O elements from their native state to $Na_2Ti_6O_{13}$ compound at activation temperature 900 °C, whereas HR-TEM evident the formation of a microporous catalyst having an average particle size 50.24 nm. The synthesized catalyst was utilized for transesterification of glycerol with DMC and was found to be very efficient. The characterization results demonstrate that the incorporation of Na on titanium oxide lattice enhances the crystallinity forming the pure phase of sodium hexatitanate, i.e., $Na_2Ti_6O_{13}$ which potentially showed its activity towards glycerol carbonate production. On the basic of basicity test, it can be concluded that basicity plays a major role in the conversion of glycerol-to-glycerol carbonate as in spite of not having quite an appreciable surface area, sodium hexatitate catalyst shows remarkable performance in transesterification of glycerol. The catalytic activity of prepared $Na_2Ti_6O_{13}$ was evaluated through NMR spectroscopic analysis of the synthesized product and disclosed a good efficiency in mild reaction conditions with 98.5% conversion and 94.5% yield. A plausible mechanism was explained on the basis of L-H mechanism and previous reports. The catalyst endurance test consisting of reusability and turn over frequency were also determined and shows that catalyst is reusable for five consecutive runs. In addition, green metric parameters calculated for synthesized catalyst reveals its atom efficiency, non-toxicity, and environmentally friendly nature. This shows the potency of sodium hexatitanate catalyst towards the economically viable production of glycerol carbonate and biodiesel.