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## **Chapter 2**

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# **Experimental Procedures and Characterization Techniques**

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## **2.1. Introduction**

This chapter illustrates the methods adopted for designing, characterization and assessment of their catalytic activity towards transesterification of glycerol. The basic fundamental and operating conditions of different characterization techniques like Thermo-gravimetric analysis and differential scanning calorimetry (TGA – DSC), X-ray diffraction pattern (XRD), Field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray analysis (EDAX or EDX), Transmission electron microscopy (TEM) with high resolution micrograph analysis along with SAED pattern studies, Fourier transform infrared spectroscopy (FT-IR), Basicity measurement using Hammett indicator titration and X-ray photoelectron spectroscopy (XPS) were used to characterize the catalysts used in proposed studies.

## **2.2. Reagents and catalysts**

All the chemicals namely  $\text{TiO}_2$  (AR grade),  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{NaNO}_3$ ,  $\text{NiNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ , titanium isopropoxide,  $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2\cdot 9\text{H}_2\text{O}$ , DMC (99.0 wt.%), Glycerol (99.0 %), etc. were acquired from Merck Limited, India. Ammonium hydroxide, Dimethyl carbonate, t-butanol, methanol, hydrochloric acid,  $\text{DMSO-d}_6$  were taken from S. D. fine chem Limited, New Delhi, India and used as such in the experiments. Catalysts like  $\text{Li/TiO}_2$ ,  $\text{Na}_2\text{Ti}_6\text{O}_{13}$ ,  $\text{Ni/CaO}$ ,  $\text{Mg/CuO}$ ,  $\text{Mg/MnO}_2$  were synthesized in laboratory by simple wetness impregnation method and co-precipitation methods.

## **2.3. Methods for preparation of catalyst**

### **2.3.1 Wet impregnation method**

This method is simple and commonly used for synthesizing heterogeneous catalysts. In this method, a certain volume of the active metal salt precursor is dissolved in an excess of organic or an aqueous solvent. After that, the active metal solution is poured to a same volume of solution

containing catalyst support with a previously weighed solid support. Capillary action starts which pulls the active metal solution into the pores of the support. A slower diffusion method is used to transport the solution when there is a surplus of the support pore volume added. The catalyst was then dried and calcined to deposit the metal on its surface while removing the volatile component that was present in the solution. The mass transfer inside the pores during impregnation and drying determines the concentration profile of the active metal component.

### **2.3.2 Co-precipitation method**

One of the most used preparation techniques is precipitation, which can be used to make supports, single component catalysts, mixed catalysts, or catalysts with several components. The catalyst constituents can be extensively stirred using either the creation of mixed crystallites comprising the very small crystals or the extremely small crystal constituents. The pH of the solution must be maintained at the required level and corrected during precipitation. Due to their low toxicity, hydroxides and carbonates are the preferred precipitates which increases solubility.

After preparation of catalyst through impregnation or co-precipitation, the catalysts undergone to:

(i) Drying and (ii) Calcination

#### **(i) Drying**

Catalyst's sample drying is the method of eliminating solvent, typically water, from the solid's pores. For crystalline solids, this is a standard technique, but it becomes crucial for flocculates and much more so for hydrogels, which can contain up to 90% water. When this occurs, the elimination of water might cause the texture to collapse, thus drying must be done correctly. For materials that have a comparatively higher adsorption capacity (high porosity), drying conditions have no impact on the consistent dispersion of the driving force. Low-adsorption-capacity (catalysts with low-porosity) impacts the texture and characteristics of the resultant catalysts. The speed of evaporation

must be gradual and reversible in order to agree redistribution of the active components uniformly on the support's surface of the catalyst.

### **(ii) Calcination**

Calcination, which is an auxiliary heat treatment further than drying, is defined as heating without the creation of a liquid phase. It takes place in the presence of air at temperatures greater than those of the catalytic process. Several chemical and physical processes, including changes like the impregnated metal salt breaking down into its oxide, sintering of the support, interaction between the active components and support. The condensation of the support's hydroxyl groups also takes place during the heating. The catalyst used in calcination converted into a form, for instance, amorphous form into crystalline form. During this procedure, the catalyst's physicochemical and mechanical properties are mostly produced [98].

## **2.4. Methods adopted for catalyst designing in present work**

### **2.4.1. Synthesis of Li/TiO<sub>2</sub>**

By using a wetness-impregnation technique, followed by a subsequent thermal treatment, a heterogeneous catalyst made of Li/TiO<sub>2</sub> was created. In the beginning, the necessary volume of double distilled water was used to dissolve a solution of pure TiO<sub>2</sub>. The needed quantity of LiOH was dissolved in distilled water according to the loading percent to create the LiOH solution. The remaining water was evaporated at 120 °C while swirling continuously until xerogel was formed after mixing the two solutions continuously for 12 hours. The subsequent white solid was dried up for 12 hours at 110 °C, and the catalyst was then calcined for 4 hours in an air-flowing muffle furnace at 650 °C.

### 2.4.2 Synthesis of Na/TiO<sub>2</sub>

The Na-promoted TiO<sub>2</sub> based catalysts were made using both the precipitation method and the wetness incipient approach at room temperature. Sodium hexatitanate catalyst was made by adding sodium nitrate solution to titanium isopropoxide solution during the wetness incipient method. Titanium isopropoxide powder was impregnated with saturated sodium nitrate solution after the necessary amount of sodium nitrate was made as a saturated solution and dissolved in double distilled water. To ensure that the ions were dispersed as far as possible into the precursor molecules, the resulting mixture was continuously stirred at 80 °C for 1 hour, followed by 8 hours at ambient temperature. The mixture was then heated to 80 °C while being stirred continuously at 500 rpm to remove extra water and turn it into xerogel, or slurry-like material. The xerogel was dried overnight in a hot air oven set at 120 °C. The dried sample was subjected to heat treatment at various temperatures for 5 hours each. The synthesized catalysts having varied Na contents are created and named as 5TNO, 10TNO, and 20TNO.

### 2.4.3 Synthesis of Ni/CaO

CaO nanoparticles were originally designed using distillation waste. In order to obtain the pure raw material, the collected distillation waste was centrifuged and repeatedly cleaned with ethanol and double distilled water. Using a mortar and pestle the raw material was made fine and dried in an oven for 12 hours. The resulting material was then subjected to additional thermal treatment of 800 °C for 4 hours. After the reaction was finished, a sample was obtained and powdered once again for use as a CaO precursor. Nickel metal nitrate salts were added to the resulting CaO. The catalysts that were obtained were designated as NDW. The aforementioned catalysts were created using the wetness impregnation approach in order to explore how the catalyst synthesis process altered the phase and activity of the NDW catalyst. The catalyst, known as NDW, was initially

created using a 2:1 Ni/Ca atomic ratio. The obtained catalyst is calcined at 700 and 900 °C to produce NDW@700 and NDW@900, respectively.

#### **2.4.4. Synthesis of Mg/CuO and Mg/MnO<sub>2</sub> catalyst.**

The co-precipitation method was used to synthesize the mixed oxides of magnesium with various transition metals, such as Mg/CuO and Mg/MnO<sub>2</sub>, while maintaining a consistent pH range of 8 to 10. First, the necessary quantity of magnesium nitrate was added to a beaker and mixed with the correct amount of double distilled water. A precise quantity of manganese acetate was taken and dissolved in double distilled water in a different beaker. Both solutions were combined and stirred at 40 °C (Mg: Mn molar ratio equal to 1:2 in the reaction mixture). Ammonia solution (ammonium hydroxide) was drop-by-drop added during the reaction procedure to keep the pH between 8 and 10 while also enabling precipitation. The reaction mixture was agitated for an additional 5 hours after the precipitation formed in order to promote the precipitate phase's selective growth. The resultant combination was next filtered and repeatedly rinsed with water to remove any contaminants. Further, the solid sample was calcined at 400 °C for 5 hours in an air muffle furnace after being stored in a hot air oven at 110 °C for 12 hours. Finally, the finished product was removed from the furnace, crushed, and sieved to obtain the fine catalyst powder. The resulting catalyst was kept and then utilised to transesterify glycerol to glycerol carbonate. Similar to this, Mg/CuO was also produced and tested in the transesterification of glycerol.

Different characterization approaches were used to assess the catalyst stability and different physicochemical properties of the catalyst, and a transesterification reaction with glycerol was used to assess the performance of the catalyst.

## 2.5. Characterization of catalysts

### 2.5.1. TGA-DSC

Two analytical methods for thermal investigation include thermogravimetric and differential scanning calorimetric analysis. This technique was used to determine the mass transformation as a function of temperature while maintaining a uniform heating rate or time and a constant mass loss. Basically, TGA analysis was done to ascertain the catalyst's stable temperature, which refers to the temperature at which it can be calcined to obtain the stable catalyst. The thermal stability was investigated by thermal gravimetric analysis (TGA) and Simultaneous Thermal Analyzer STA 6000 (PerkinElmer Pvt. Ltd) instrument with a varying temperature range from 50 °C to 700 °C using heating ramp rate at 10 °C-min<sup>-1</sup>.

### 2.5.2. XRD

XRD is the most potent, popular, and flexible technology for the qualitative and quantitative investigation of the solid catalyst sample phase and offer details on the catalyst particle size of certain components. It is also used to determine a material's structure, allotropic transformation, transition to distinct phases, material purity, lattice parameters, and the presence of external atoms in the crystal lattice of an active component [99]. The diffraction patterns of the prepared catalyst were investigated on X-Ray diffractometer instrument (Rigaku miniflex) using Ni filtered Cu K $\alpha$  radiation as the X-ray source having wavelength 1.5406. The applied voltage was 30 kV and 15 mA. The X-ray diffraction pattern was measured within 10° to 80° 2 $\theta$  range with 5° min<sup>-1</sup> scanning rate and 0.02° step function.

### 2.5.3 FT-IR Spectroscopy

At specific quantized energy levels, the atoms present in a molecule shows rotation and vibration in various ways. A molecule's infrared spectrum is the result of its atoms' vibrations and rotations,

which affect the molecule's permanent dipole moment. The different functional groups of the active component and the support have been thoroughly identified using infrared spectroscopy. The surface functional group of the designed catalyst was analysed by FT-IR analysis performed on FT-IR Nicolet 5700 spectrometer in the range of 4000 – 400  $\text{cm}^{-1}$  using KBr pellet.

#### **2.5.4. XPS Spectroscopy**

When it comes to conducting chemical analyses, XPS, or X-ray photo electron spectroscopy, is commonly used. The elemental existence, empirical formula, oxidation state, chemical state and electronic state of a catalyst's constituent elements can all be ascertained using XPS. By shining an X-ray beam on a solid surface and evaluating the kinetic energy of the electrons that are emitted from the top 1 to 10 nm of the sample under study, the spectra are created. The XPS was performed by K-Alpha (Thermo Fisher Scientific) spectrometer fitted with aluminium ( $\text{Al } k\alpha$  radiation) monochromator source having energy 1486.7 eV operated at 15 kV and 20 mA. By taking the  $\text{C}1s$  peak (284.6 eV) as a reference, the binding energy of all recognized elements was standardized.

#### **2.5.5. SEM-EDX**

SEM analysis is used to evaluate the surface shape, catalyst particle size, and various inorganic and organic substances. By refocusing an electron beam through the sample's surface and collecting secondary or backscattered electron signals, scanning electron microscopy can provide detailed resolution images of the sample. Element detection and quantitative compositional information are also acquired by an energy dispersive X-ray analyser (EDX or EDAX). SEM offers images with a magnification of up to X50,000, making it possible to observe features that are far smaller than the optical microscope's field of view, or sub-micron-scale features. The elemental composition of a catalyst can be determined using an X-ray technique called EDX. The average



particle size, surface shape and chemical composition of the produced catalyst were all determined by NOVA Nano SEM 450 equipped with EDAX – Ametek detector [100].

### 2.5.6. TEM Analysis

The powerful tool and widely utilised method of transmission electron microscopy (TEM) is used to characterise materials. By interaction of high intensity electron beam with the atoms in the material, the electrons produce pictures that can be utilised to identify aspects like the crystal structure, its dislocations, and the limits and shapes of the grain. Transmission electron microscopes, which use de Broglie wavelengths that are a fraction of an angstrom smaller than those used in light microscopes, offer far greater resolution. Due to this characteristic of the equipment, it is feasible to capture even single atoms, which are 1,000 times smaller than an item under a light microscope. The transmission electron microscope (TEM, FEI Tecnai-20G2) used a LaB6 filament and an accelerating voltage of 200 kV to produce bright-field TEM micrographs and selected area diffraction patterns (SAED) [101].

### 2.5.7. Hamett indicator

The basicity of the catalysts was tested by titrating the solid catalysts suspended in benzene solution with benzene-benzoic acid solution (Hammett indicator method), using several indicators having  $pK_{BH^+}$  as bromothymol blue ( $H_+ = 7.2$ ), phenolphthalein ( $H_+ = 9.8$ ), 2,4-dinitroaniline ( $H_+ = 15.0$ ), and 4-nitroaniline ( $H_+ = 18.4$ ) as some indicators. In this process, 0.25 g of the prepared catalyst sample was mixed benzene (10 mL) in a ground glass stopper flask. After the thorough dispersion of the catalyst sample in benzene, it was titrated with 0.1 N benzoic acid solution in benzene until the colour change occurs. The overall basicity is expressed in  $\text{mmol g}^{-1}$ .

## 2.6. Activity study

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, 2 moles of DMC, and 0.46 g of catalyst dose (i.e. 5 wt.% of the catalyst with respect to the weight of glycerol (in g) used in the reaction matrix) 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  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, GC-MS, HR-MS analysis was performed to analyse and confirm the desired product formed.

### 2.6.1. NMR spectra

NMR technique is widely used for qualitative and quantitative analysis of different organic compounds. In this present study, the synthesized product glycerol carbonate was quantified by both proton and carbon NMR spectroscopy. The validity of the Glycerol Carbonate formed was analysed through  $^1\text{H}$  and  $^{13}\text{C}$  NMR analysis.

Using proton NMR % of glycerol conversion can be quantified using the formula:

$$\% \text{ Conversion of Glycerol, \% Gly} = \frac{I_{a1}}{I_b + I_{a2}} \times 100 \quad (2.1)$$

where,  $I_{a1}$  = Integration of one of the  $\text{CH}_2$  proton of glycerol carbonate (3.736 - 3.793 ppm) and

$I_b + I_{a2}$  = Sum of the integration of  $\text{CH}$  proton of glycerol (b) and integration of  $\text{CH}_2$  proton of glycerol carbonate ( $a_2$ ) (3.557 – 3.640 ppm).

Likewise, the different types of signals in carbon NMR spectra depicts the different type of carbon present in the glycerol carbonate moiety. The NMR spectra was quantified using the product was characterized by NMR analysis on NMR spectrometer by BRUKER 500 MHz Ascend TM 500 instrument. DMSO-d<sub>6</sub> was used as solvent and TMS as reference.

### 2.6.2. GC-MS analysis

Gas chromatography (GC) analysis with a SHIMADZU -2010 equipped with a 30m 0.25mm DB-1 WAX column was performed to quantitatively measure the product produced from the transesterification of glycerol. The oven temperature was set at 60 °C and then risen to 240 °C at a rate of 10 °C/min for the GC analysis. About 250 °C was the temperature of the injector, whereas 280 °C were the temperature of the FID. For the GC analysis of produced glycerol carbonate, tertiary butanol was used as an internal standard. The following equations are used to determine the conversion, selectivity, and yield percentage of glycerol and glycerol carbonate.:

$$\text{Glycerol Conversion (\%)} = \frac{\text{No of moles of glycerol reacted}}{\text{Total no of moles of glycerol taken}} \times 100 \quad (2.2)$$

$$\text{Selectivity (\%)} = \frac{\text{No of moles of glycerol carbonate}}{\text{Total no of moles of all products}} \times 100 \quad (2.3)$$

$$\text{Yield (\%)} = \frac{\% \text{ glycerol conv} \times \% \text{ GlyC selectivity}}{100} \quad (2.4)$$

### 2.6.3. HR-MS analysis

The composition of reactants involved in the reaction and the product formed can be evident through high-resolution mass spectroscopy (HR-MS) studies. The components before and after the glycerol transesterification reaction present in the reaction mixture were analyzed in this study. HR-MS studies were performed by SCIEX Model-X500R QTOF instrument.