CHAPTER 3

Materials and Methodology

3.1 Introduction

This chapter describes the methods adopted for the preparation, characterization and evaluation of these catalysts in transesterification of glycerol. The basic principles and experimental details of different characterization techniques like N_2 -sorption, X-ray diffraction pattern (XRD), Fourier transform infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA-DSC), Scanning electron macroscopy with energy dispersive X-ray analysis (SEM-EDX), X-ray photo electron microscopy (XPS) and Hammet indicator basicity study used to characterize the catalysts have been well explained.

3.2 Reagents and Catalysts

All the metal nitrates like $Mg(NO_3)_2 \cdot 6H_2O$, $Sr(NO_3)_2$, $Al(NO_3)_3 \cdot 9H_2O$, KNO_3, $Cr(NO_3)_3$, $VO(NO_3)_3$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2$, $Ca(NO_3)_2$, $Ti(NO_3)_4$, $Zr(NO_3)_4$ were procured from Merck Limited Mumbai, India. Ammonium hydroxide, DMSO-d_6, t-butanol, methanol, Dimethyl carbonate, Hydrochloric acid, were taken from S.D fine chem Limited, New Delhi India. Catalysts like Mg doped ZnO, NiMgOx, $MgCr_2O_4$, MgV_2O_4 were prepared in the laboratory by simple wet impregnation and co-precipitation methods.

3.3 Methods for preparation of catalysts

3.3.1 Wet impregnation method.

This is a very simple and widely used method for synthesis of heterogeneous catalysts. Typically, the active metal precursor is dissolved in an aqueous or organic solvents. Then, the metal-containing solution is added to a catalyst support containing the same volume of solution. Capillary action draws the solution into the pores. Solution added in excess of the support pore volume causes the solution transport to change from a capillary action process to a diffusion process, which is much slower. The catalyst can then be dried and calcined to drive off the volatile components within the solution, depositing the metal on the catalyst surface. The maximum loading is limited by the solubility of the precursor in the solution. The concentration profile of the impregnated compound depends on the mass transfer conditions within the pores during impregnation and drying.

3.3.2 Precipitation method

This method is also a very common method for synthesis of various type of heterogeneous catalysts. In this method a single component catalyst or mixed metal oxide catalysts were synthesized which is also known as co-precipitation method. In this process, intermixing of catalyst components can be achieved by formation of very small crystallites or formation of mixed crystallites containing the constituents. During precipitation process pH of the solution is maintained to required level and kept constant. Basically, hydroxides and carbonates are preferred precipitates as of their low solubility, easy decomposition and minimal toxicity. There are several factors which affect the properties of precipitated catalysts such as pH, precipitating agent, solvent mixing sequence, temperature, aging speed, solution composition etc. After precipitation the catalysts were subjected to (I) drying and (II) calcination.

(I)Drying

It involves mainly elimination of solvents (usually water) from the pores of synthesized catalysts. This is a routine procedure for crystalline solids but becomes critical for flocculates and even more so for hydrogels that contain up to 90%water. The removal of water can result in collapse of the texture and therefore drying has to be properly controlled if high porosity is desired. For supports with relatively high adsorption capacity (high porosity) , the condition of drying does not affect the uniform dispersion of the active component. For carriers with a low adsorption capacity, (low porosity) these parameters influence the texture as well as the properties of the resulting catalysts. The rate of evaporation has to be slow and reversible to allow even redistribution of the active components on the surface of support.

(II) Calcination

After drying, the catalyst undergoes heat treatment which is known as calcination. Calcination is mainly carried out in air at temperature higher than those used in catalytic reactions. In this process various physical and chemical transformation like decomposition of metal carbonates, hydroxides and nitrates take place to corresponding oxides by interaction between active component and support materials. During calcination, the catalyst also gets solidified into a final form like amorphous or crystalline. The surface and mechanical properties of the catalysts are derived mainly in this process.

3.4 Methods adopted in present work for catalyst designing

In present study, precipitation / co-precipitation methods of preparation were adopted to prepare metal oxide catalysts.

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

The Mg doped ZnO catalysts utilized in glycerol transesterification reaction were prepared by wet impregnation method. At first, 5g of ZnO was taken in a 100 ml beaker and then 50 ml aqueous solution of $Mg(NO_3)_2$ with appropriate amount was added to the above ZnO solution. The resulting mixture was stirred at room temperature for 10-12h. The water content in the mixture solution was removed by rotary evaporator after completion of stirring. The residual white solid was dried at 110^0C overnight in oven and then calcined at different temperatures (150, 350, 550 and 750^0C) for 5h The prepared catalysts were notified as nMg/ZnO-T, where n and T correspond to Mg loading and calcinations temperature respectively. For example, 0.03Mg/ZnO refers to 3wt%Mg supported on ZnO. similarly Mg/ZrO_2, Ba/ZnO, Sr/ZnO ,K/ZnO were prepared by simple wet impregnation method and calcined at 550^0C for 5h as like Mg/ZnO as mentioned above. All the prepared catalysts were applied for glycerol carbonate synthesis.

3.4.2 Synthesis of bimetallic NiMgOx catalyst

MgNi catalysts with various molar ratios (Mg/Ni=1:1, 2:1, 3:1) were synthesized taking respective stoichiometric amounts by the co-precipitation route. For the synthesis of different catalysts, the required amount of Mg $(NO_3)_2 6H_2O$ and Ni $(NO_3)_2 .6H_2O$ were dissolved separately using deionized water. The prepared solutions were mixed in a single beaker and allowed to continuous stirring at room temperature for 6-7 h. After that the temperature of the stirred solution was raised to 50°C with dropwise addition of liquid ammonia solution to maintain the pH of the solution 10-12. The reaction mixture was undergone further stirring to get a better precipitate. After complete precipitation it was filtered and washed with deionized water several times for obtaining the desired catalyst, the synthesized catalyst was kept in an oven at 110°C for 10-12 h and calcined in a muffle furnace at 700°C. The prepared catalysts were specified according to molar ratio and calcinations temperature as m: n NiMg –T where m and n indicate the molar ratio of nickel and magnesium respectively, T refers to calcination temperature.

3.4.3 Synthesis of transition metal-based spinels of MgO

The mixed oxides of magnesium with different transition metals like $MgCr_2O_4$, MgV_2O_4, were synthesized via co-precipitation route at constant pH range 8-10 using metal nitrate as precursors. First of all, required amount of magnesium nitrate was taken in a beaker and dissolved in appropriate amount of de-ionized water. In another beaker specific amount of chromium nitrate was taken and dissolved with deionized water. Both the solutions were mixed and undergoes stirring at 40°C (Mg: Cr molar ratio equal to 1:2 in the reaction mixture). During the reaction process, there was dropwise addition of ammonia solution (ammonium hydroxide) in order maintain the pH 8-10 as well as to allow precipitation. After formation of precipitate, the reaction mixture was also stirred for another 5h to enhance the selective growth of precipitate phase. Then the product mixture was filtered, washed with water several times in order to remove any impurities. After that the solid sample was kept in oven at 110°C overnight and then calcined at 900°C for 4h in a muffle furnace. Finally, the resultant product was collected from the furnace and crushed and sieved to get the fine powder of catalyst. The obtained catalyst was stored and further used in transesterification of glycerol. Similarly, another catalyst i.e., MgV_2O_4, was also synthesized and tested in transesterification of glycerol.

3.5 Characterization of designed catalyst

The physicochemical properties of synthesized catalysts were studied by several characterization techniques like TGA-DSC, XRD, XPS, FT-IR, SEM-EDX, BET-surface area, Hammett indicator method etc.

3.5.1 TGA-DSC

Thermogravimetric (TGA)-Differential scanning calorimetry (DSC) is an analytical method of thermal analysis. It was used to measure the mass transformation as a function of temperature (at constant heating rate) or time (at constant temperature and mass loss). The TGA analysis was performed to find out the calcination temperature of powder material obtained in catalyst preparation. The temperature measurement was accomplished in the presence of air and change in mass was recorded with increasing temperature. During heating process, sample can lose weight by expulsion of volatile matter (moisture) or various gases. The obtained data was plotted between weight percent (%) and temperature (°C). TGA was performed on METTLER TOLEDO 1* instrument in oxidative atmosphere of mixture of air and inert gas. Maximum temperature was chosen for stability of sample implies the completion of all chemical reactions. The sample starts heating with the rate of 20 ºC/min starting from 50 ºC to 1000 ºC temperature range. Resulting curve obtained was steeper with close onset temperature

3.5.2 X-ray diffraction pattern (XRD)

The qualitative and quantitative analysis such as crystallite size, crystal orientation, particle size, different phases of the synthesized catalysts were studied by X-ray diffraction pattern (XRD). It can also helpful in study of structure of substance, transition to different phase, its allotropic transformation, lattice constant, purity of the substance and presence of foreign atoms in the crystal lattice of active component. The interaction of X-ray with periodic structure of polycrystalline material created the diffraction pattern in the compound. In this technique a fixed wavelength is selected for incident radiation and Bragg peaks are measured by observing the intensity of scattered radiation as a function of angle 2θ . The inter planner distance (d- spacing) are calculated from the value of peaks observed from Bragg's equation.

$$\mathbf{n\lambda = 2d\sin\theta} \qquad (3.1)$$

where n is the order of reflection and the values are 1,2,3……

X-ray diffraction is also beneficial for determining the atomic position and number of shells present in the compound. The d values are tabulated in decreasing order and relative intensities are recorded on a scale of 100 for strongest line. Indicating XRD peaks as the strongest, 2nd strongest, 3rd strongest etc, d -values are termed as d_1, d_2, d_3 etc matched with standard ASTM/JCPDS values for the crystal structure. In this work, the XRD pattern of synthesized catalysts were recorded on a Rigaku miniflex X-ray diffractometer using Ni filtered Cu Kα radiation having wavelength 1.5406A° with a scan rate of 2° min^{-1} and scan range of 10-90 at 30kV and 15mA .

3.5.3 FT-IR spectra

It is a very simple technique to determine the surface functional groups present in synthesized catalysts. The infrared spectrum of a molecule mainly arises due to vibration and rotation of atoms in different ways at certain quantized energy level in a molecule. There is creation of change in dipole moment in the molecule due to change in rotational and vibrational motion. The most commonly used wave number region lies in the range of 400 to 4000cm^{-1} FT-IR spectra provide valuable information like nature of atoms, stretching band, bending vibration band, spatial arrangement and their chemical linkage forces, various functional groups present in both active and support species etc. The surface basicity of the component is also characterized by FT-IR spectra. There are different ways to prepare the sample for FT-IR study. The catalyst in powder form is commonly prepared as thin pellet in order to be transparent to infrared beam. KBr pellets are also prepared for verification of metal oxide structure through grinding 2mg catalyst with 200 mg KBr. In the present study, the FT-IR spectra of synthesized catalyst and GLC were recorded via using Nicolet 5700 spectrometer by KBr pellet method.

3.5.4 SEM-EDX

The surface morphology, particle size of catalysts, many organic and inorganic compounds are investigated through scanning electron microscopy (SEM)analysis. SEM provides detailed high-resolution images of the sample by restoring a focussed electron beam across the surface and detecting secondary or backscattered electron signal. An Energy Dispersive X-Ray Analyzer (EDX or EDA) is also used to provide elemental identification and quantitative compositional information. SEM provides images with magnifications up to ~X50,000 allowing sub-micron-scale features to be seen i.e., well beyond the range of optical microscopes. Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an X-ray technique used to identify the elemental composition of materials or catalysts. In a multi-technique approach, EDX becomes very powerful, particularly in contamination analysis and industrial forensic science investigations. The technique can be qualitative, semi-quantitative, quantitative and can also provide spatial distribution of elements through mapping. The EDX technique is non-destructive and specimens of interest can be examined in situ with little or no sample preparation. In present work, the surface morphology and elemental composition of synthesized catalysts were detected through field emission scanning electron microscope (FE-SEM) NOVA Nano SEM 450 equipped with EDAX-Ametek detector.

3.5.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) commonly known as electron spectroscopy for chemical analysis (ESCA). It is simple phenomenon for analysing the surface chemistry of a material. XPS can measure the elemental composition, empirical formula, chemical state and electronic state of the elements within a catalyst and material. XPS spectra are obtained by irradiating a solid surface with a beam of X-rays while simultaneously measuring the kinetic energy of electrons that are emitted from the top 1-10 nm of the material being analysed. A photoelectron spectrum is recorded by counting ejected electrons over a range of electron kinetic energies. Peaks appear in the spectrum from atoms emitting electrons of a particular characteristic energy. The energies and intensities of the photoelectron peaks enable identification and quantification of all surface elements. A typical XPS spectrum is a plot of the number of electrons detected at a specific binding energy. Each element produces a set of characteristic XPS peaks. These peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1*s*, 2*s*, 2*p*, 3*s*, etc. The number of detected electrons in each peak is directly related to the amount of element within the XPS sampling volume. To generate atomic percentage values, each raw XPS signal is corrected by dividing the intensity by a *relative sensitivity factor* (RSF), and normalized over all of the elements detected. Since hydrogen is not detected, these atomic percentages exclude hydrogen. In this present work surface oxidation state and binding energies of the atoms present in synthesized catalysts were explored by ESCA X-ray photoelectron spectroscopy (XPS) equipped with aluminium monochromator source (Al kα radiation) having energy 1486.7eV operated at 15kV and 20mA.

3.5.6 BET surface area

The textual characteristics like surface area, pore volume and pore size of solid samples are determined by gas adsorption technique (N_2 adsorption desorption technique). The specific surface area of synthesized catalysts was studied by BET (Brunner, Emmet and Teller) method at their boiling temperature. The significance of BET theory lies in its ability to determine the number of molecules required to form a monolayer of adsorbed gas on a solid despite the fact that a mono molecular layer is never actually formed. The basic equation for finding out surface area by BET method is given by

$$\frac{P}{Va\,(P0-P)} = \frac{1}{Vm\,C} + \frac{(C-1)P}{Vm\,C\,P0} \qquad (3.2)$$

Where P_0 = Saturated vapour pressure of the adsorbent, mmHg

P = Equilibrium adsorption pressure mmHg

V_a = volume adsorbed at STP at pressure p.

V_m = Volume adsorbate required to form a monolayer coverage, ml STP.

C = constant related to heat of adsorption

Plotting a graph of P/ $V_a(P_0\text{-}P)$ versus relative pressure P/P_0 a straight line was obtained with slope of $(C\text{-}1)/(V_mC)$ and intercept about $1/(V_mC)$ respectively. Subsequently the specific surface area of the sample can be determined by the equation as

$$\text{Specific surface area } (m^2/g) = \frac{Vm\,NA}{22141\times wt} \times A \qquad (3.3)$$

Where N_A is the Avogadro number (6.023×10^{23})

Vm is monolayer volume in ml at STP.

wt. is the weight of the catalyst in gm.

A is the cross-sectional area of adsorbate molecule ($16.2A^{o2}$ for N_2 molecule)

The specific surface areas of the synthesized catalysts were studied by N_2 desorption at -196°C using a commercial multipoint Micromeritics ASAP2000. Around 0.2 mg of sample was used for analysis where the moisture and other adsorbed gases present in the sample were removed before the analysis by degassing the sample at 200°C for 2h. The sample was evacuated at 2.67Pa before N_2 adsorption.

3.5.7 Basic strength by Hammet Indicator method

The basic sites and basicity of heterogeneous catalyst play major role in transesterification of glycerol, as a result it is highly required to study the basic strength and basicity of synthesized catalyst. In this work, the basicity study of synthesized catalysts was done by simple Hammett indicator titration method. The indicators like bromothymol blue ($H\_ =7.2$), phenolphthalein ($H\_ = 9.8$), 2,4- dinitroaniline ($H\_ = 15.0$) , 4-nitroaniline ($H\_ = 18.4$) were used in titration method. Around 25mg of catalyst was taken and stirred with 1.0cm^3 of Hammett indicator solution diluted with methanol and kept for 2h to equilibrate. After a certain time, there was change in colour of indicator solution implying the catalyst is stronger base than indicator. The overall basicity of synthesized catalyst was quantitatively calculated by benzene carboxylic acid titration method taking 0.1 N benzoic acid dissolved in benzene used as titrant. The overall basicity is expressed in mmolg^{-1}.

3.6 Activity study

Glycerol carbonate was synthesized in liquid phase at atmospheric pressure, temperature range 60-90°C via reflux condensation process. Adequate amount of glycerol and DMC were taken in a round bottom flask and certain amount of catalyst was added to the reaction mixture and undergone stirring with required temperature and time. After completion of reaction the product mixture was separated by filtration and then undergone rotary evaporator to evaporate the solvent like methanol or DMC present in the product mixture. Finally, glycerol carbonate was obtained as single product, the conversion, yield and selectivity percentage of glycerol and GLC respectively were calculated using gas chromatography and ^{1}HNMR spectra.

3.6.1 Gas chromatography (GC-FID)

The product obtained from transesterification of glycerol was quantitatively measured by gas chromatography (GC) analysis using SHIMADZU -2010 equipped with 30m × 0.25mm DB-1WAX column. GC analysis was carried out using following temperature programme as the oven temperature was 60°C and then increased to 240°C at a rate of 10°C /min. The injector temperature was about 250°C, whereas FID temperature was about 280°C. Tertiary butanol was used as internal standard for GC analysis of synthesized glycerol carbonate. The conversion, selectivity and yield percentage of glycerol and GLC are calculated using following equations as

$$\text{Glycerol Conversion (\%)} = \frac{No\ of\ moles\ of\ glycerol\ reacted}{Total\ no\ of\ moles\ of\ glycerol\ taken} \times 100 \qquad (3.4)$$

$$\text{Selectivity (\%)} = \frac{No\ of\ moles\ of\ desired\ product}{Total\ no\ of\ moles\ of\ all\ products} \times 100 \qquad (3.5)$$

$$\text{Yield (\%)} \ = \ \frac{\%\ \boldsymbol{glycerol\ conv} \times\ \%\ \boldsymbol{GLC\ selectivity}}{\mathbf{100}} \qquad (3.6)$$

3.6.2 NMR Spectra

NMR technique is a simple and widely used technique for qualitative and quantitative analysis of many organic products. In this work, the synthesized glycerol carbonate was quantified by both proton and ^{13}C NMR spectroscopy. Using proton NMR spectra, the conversion percentage of glycerol was also calculated by the following equation as

$$\text{Conversion (\%)} = \frac{b'CH}{bCH + b'CH} \times 100 \qquad (3.7)$$

Where b'_{CH} and b_{CH} are the integration of the methine protons of glycerol carbonate and glycerol, respectively.

Similarly, the different types of chemical shift values for different types of carbon confirmed the formation of glycerol carbonate. NMR spectra of synthesized product was quantified using BRUKER 500mHZ Ascend TM 500 (advance IIIHD) instrument and DMSO-d_6 was used as solvent and TMS as reference.