CHAPTER 3

Materials and Methodology

3.1 Introduction

This chapter deals with the methods adopted for synthesis, characterization, and catalytic evaluation of their catalytic activity in glycerol acetalization. The characterization of synthesized catalyst was done by various techniques like X-ray diffraction pattern (XRD), Thermo-gravimetric analysis and differential scanning calorimetry (TGA-DSC), N_2-adsorption-desorption isotherm, Field emission scanning electron microscopy (FE-SEM) with energy dispersive X-ray analysis (EDAX), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and Boehm titration method have been explained in proposed studies.

3.2 Reagents and Catalysts

All the precursor chemicals, namely $ZrO(NO_3)_2.H_2O$, $Al(NO_3)_2.9H_2O$, $Co(NO_3)_2.6H_2O$, and titanium dioxide, were procured from Merck Limited, India. An aqueous solution of ammonium hydroxide, 1,4-dioxane, acetone, DMSO-d6, sulfuric acid, hydrochloric acid, sodium hydroxide, and sodium chloride was purchased from SD Fine-chem Limited, New Delhi, India. All the chemicals were used without any further variations. Catalysts like SO_4^{-2}/ZrO_2-Al_2O_3, $SO_4^{-2}/CoAl_2O_4$-TiO_2, and $SO_4^{-2}/ZnAl_2O_4$-ZrO_2 were synthesized in the laboratory via co-precipitation and wetness impregnation methods.

3.3 Methods for Catalyst Synthesis

3.3.1 Wet impregnation method

This approach is simple and widely employed for the synthesis of heterogeneous catalysts. In this procedure, a specific amount of active metal precursor is dissolved in excess of the organic or aqueous solvent. Subsequently, the solution of active metal is poured into an equal volume of the active support solutions. With the help of capillary action, the active metal solutions draw the pores of the support. When an excess of support solution is added, a slower diffusion method is employed to transport the solution.

Furthermore, the catalyst underwent drying and calcination to deposit the metal on the surface of the catalyst while eliminating the volatile component that was present in the solution. During the impregnation and drying process, the concentration profile of the active metal component is determined by the mass transfer within the catalyst's pores.

3.3.2. Co-precipitation method

This method is very common and can be used in the synthesis of single-component catalysts and mixed metal oxide catalysts. In this method, metal nitrate precursors were taken in a stoichiometric ratio and dissolved in deionized water. The constituent of the catalyst formed the mixed crystallites containing either small crystals or mixed crystals containing extremely small constituents. It is important to maintain the pH of the solution at the desired level and adjust it as necessary during the precipitation. Hydroxides and carbonates are preferred as precipitates due to their low solubility, less toxicity, and easy decomposition.

After precipitation and wet impregnation of the catalyst, the synthesized catalyst was exposed to:

(i) Drying and (ii) Calcination

(i) Drying

This process mainly involves the elimination of excess solvents, usually water, from the pores of solid synthesized catalysts. This is a standard technique for crystalline solids, but it becomes more critical for flocculates and even more so for hydrogels, which may hold as 90 % water. In such cases, removing water can potentially lead to a collapse in the texture; therefore, to gain a high porosity of material, drying must be controlled appropriately. For materials with relatively high adsorption capacity, i.e., high porosity, the drying conditions have no effects on the uniform dispersion of the effective component. However, the materials have low adsorption capacity, i.e., the catalyst with

low porosity significantly affects both the texture as well as characteristics of the resultant catalyst. The evaporation rate should be gradual and reversible to facilitate uniform redistribution of the active components across the surface of the material.

(ii) Calcination

After drying, the calcination process is performed under the heat treatment without converting to a liquid phase. It is performed under high temperatures in the presence of air than those used in the catalytic process. During the calcination process, physical and chemical transformation occurs, such as the decomposition of the carbonates, nitrated, and hydroxides into their respective oxides, sintering of the material, and interaction between the active components and support. During calcination, the catalyst undergoes solidification into a definitive form of phase, such as amorphous or crystalline. Throughout this process, the catalyst undergoes substantial changes in the surface and mechanical properties.

3.4 Methods adopted for catalyst designing in the current study

3.4.1 Synthesis of SO_4^{-2}/ZrO_2-Al_2O_3 catalyst

SO_4^{-2}/ZrO_2-Al_2O_3 catalyst utilized in solketal synthesis was prepared by co-precipitation and then followed by a wetness impregnation process. Firstly, crucial amounts of $ZrO(NO_3)_2.H_2O$ and $Al(NO_3)_2.9H_2O$ were taken and dissolved in distilled water. The prepared solution was mixed in a single beaker and stirred at room temperature for 5-6 h. After that, the temperature of the mixture increased up to 50 ^oC with the dropwise addition of liquid ammonium hydroxide solution to maintain the 8-9 pH of the solution. After precipitation, the solution was further allowed to stir till the solution became homogeneous. The obtained precipitate was filtered to remove the unwanted impurities and washed several times with distilled water. The obtained catalysts were kept in a hot air oven for 12-14 h at 383K. Then, it was calcined in an air muffle furnace for 4 h at 800

^{o}C to obtain ZrO_2-Al_2O_3 (ZA). Further modifications were needed to increase the acidity of the catalyst. The appropriate amount of synthesized ZA was immersed in a 0.5 M H_2SO_4 solution via a wetness impregnation process. Subsequently, it was dried at 110 ^{o}C overnight and further calcined in a muffle furnace in the presence of air at 550 ^{o}C for 3 h to get the final modified SO_4^{-2}/ZrO_2-Al_2O_3 (SZA) catalyst. All the synthesized catalysts were applied for the glycerol acetalization reaction.

3.4.2 Synthesis of SO_4^{-2}/$CoAl_2O_4$-TiO_2 catalyst

SO_4^{-2}/$CoAl_2O_4$-TiO_2, an acid heterogeneous catalyst, was prepared by co-precipitation, followed by the simple impregnation process. Initially, $CoAl_2O_4$ was synthesized via a co-precipitation process using metal nitrate precursor at a constant pH range. First of all, the required amount of cobalt nitrate and aluminum nitrate with a molar ratio of 1:2 was taken in a separate beaker and dissolved in distilled water. The solution was mixed in a single beaker and constantly stirred for 3-4 h at 35 ^{o}C. Dropwise addition of ammonia to maintain the pH of the solution ~ 8-10. After precipitation, the reaction mixture was left under continuous stirring overnight. Then, the precipitate was filtered out from the mother liquor and washed with distilled water to remove impurity ions. The precipitate was dried overnight at 90 ^{o}C in an oven and then calcined at 700 ^{o}C in a muffle furnace for 5 h to obtain the $CoAl_2O_4$. After that, a considered amount of $CoAl_2O_4$ and TiO_2 were mixed in a single beaker, dissolved with distilled water, stirred for 3 h at 40 ^{o}C, and then evaporated the mixture at 80 ^{o}C. The required powder was incorporated with 0.5 M H_2SO_4 solution to enhance the acidic properties of the designed catalyst by impregnation process for 4-5 h. Afterward, the final powders were dried in an oven at 110 ^{o}C and then calcined at 500 ^{o}C in an air muffle furnace for 3 h to get the desired SO_4^{-2}/$CoAl_2O_4$-TiO_2 catalysts. The different mass ratios of $CoAl_2O_4$ and TiO_2 were named as including SO_4^{-2}/$CoAl_2O_4$ (1:0) (SC), SO_4^{-2}/$CoAl_2O_4$-TiO_2 (3:2) (SCAT 3:2), SO_4^{-2}/$CoAl_2O_4$-TiO_2 (2:3)

(SCAT 2:3), $SO_4^{-2}/CoAl_2O_4$-TiO_2 (4:1) (SCAT 4:1), $SO_4^{-2}/CoAl_2O_4$-TiO_2 (1:4) (SCAT 1:4) and SO_4^{-2}/TiO_2 (0:1) (ST), respectively. The obtained catalyst was stored in a desiccator for further application in solketal synthesis.

3.4.3 Synthesis of $SO_4^{-2}/ZnAl_2O_4$-ZrO_2 catalyst

The coprecipitation and wet impregnation techniques were utilized in the synthesis of solid acid heterogeneous catalysts, specifically $SO_4^{-2}/ZnAl_2O_4$-ZrO_2 and $SO_4^{-2}/ZnAl_2O_4$-TiO_2, named SZZ and SZT, respectively. At first, $ZnAl_2O_4$ was synthesized by the co-precipitation process using nitrate salt as a precursor. In this procedure, the required quantity of zinc nitrate and aluminum nitrate was taken and dissolved in deionized water separately (Zn: Al is 1:2). At 30 ^oC, both the solutions were mixed and stirred for 3-4 h. with the adding ammonium hydroxide solution drop by drop to regulate the solution's pH within the range of 8-10. The resulting solution mixture was agitated additionally for 5-6 h. to promote selective precipitation growth. Following filtration, the reaction mixture was rinsed with distilled water three to four times to eliminate any remaining impurities. The solid mixture was then placed in a hot air oven at 120 ^oC for 8 h. and subsequentially calcined at 700 ^oC for 5 hr. in an air muffle furnace to get the desired spinel. Then, the stipulated amount of $ZnAl_2O_4$ was immersed in deionized water and added to ZrO_2. In order to augment the acidic strength of the synthesized catalyst, the mixture powder was emersed with 0.5M H_2SO_4 for 5-6 h. at 550 rpm by wetness impregnation. Afterward, the white powder underwent heat treatment in an oven overnight at 90 ^oC and was then calcined at 550 ^oC in an air muffle furnace for intervals of 3 h. intervals with a 10 ^oC/min heating rate to get $SO_4^{-2}/ZnAl_2O_4$-ZrO_2. Finally, the calcined catalyst was ground with mortar and pestle, stored in a desiccator to prevent moisture, and further applied for the acetalization reaction. Another acetalization catalyst, like $SO_4^{-2}/ZnAl_2O_4$-TiO_2, was also created and tested similarly, as discussed above.

The initial information about the stability and various physiochemical properties of the catalyst was analyzed by employing various characterization techniques. Furthermore, an acetalization reaction was performed to evaluate the catalyst performance.

3.5 Characterization of synthesized catalyst

3.5.1 TGA-DSC analysis

Thermogravimetric analysis- differential scanning calorimetry (TGA-DSC) is a catalyst with temperature-dependent physiochemical properties. This method was employed to monitor the change in mass as a function of temperature while maintaining a constant heating rate or time and a constant mass loss. TGA analysis was performed to determine the stable temperature of the catalysts, which indicates the temperature at which the catalyst can be calcined and produce a stable phase. The change in mass loss was recorded by increasing the temperature in the presence of an inert atmosphere. The sample can lose weight with an increase in temperature by the expulsion of volatile matter (like moisture) or several gases, and obtained data plotted between temperature in oC vs. weight loss in % form. The thermal stability of the uncalcined catalyst was examined using TGA PerkinElmer STA-6000 on varied temperature ranges from 10 to 1000 ^{o}C with a 10^{o}/min heating ramp.

3.5.2 X-ray diffraction (XRD)

The X-ray diffraction pattern was used to determine the qualitative and quantitative analysis of particle size, crystallite size, and orientation of the different phases of the synthesized catalyst. This method is also used to analyze the structure of material, different phase transitions, lattice parameters, detect allotropic transformation, purity of the material, and incorporation of the foreign atoms into the crystal lattice of an active component. The inter-planner distance (d-spacing) of the peaks is calculated by using Bragg's equation,

$$n\lambda=2d\sin\theta \quad (3.1)$$

where n = 1,2,3…., and indicates the order of the reflection

This method involves choosing a specific wavelength for incident radiation, and the obtained Bragg's peak is determined by analyzing the scattered radiation intensity in relation to the angle 2θ. The diffraction pattern of the synthesized catalyst was examined using a Rigaku Miniflex 600 Desktop using Cu-Kα radiation as the source of X-ray with a wavelength of 1.5406 Å. The diffractogram was recorded at a 2θ range of 5°-90° with 5°/min scan rate and a step function of 0.02° at 30 kV and 15 mA. The obtained data matched with the database of standard JCPDS files no. to confirm the phase of the synthesized catalyst.

3.5.3 Fourier-Transform Infrared (FTIR) spectroscopy

This technique is crucial for absorption spectroscopy, which thoroughly tells about the existence of different functional groups present in both active and support species. These spectra arise due to the presence of atoms within a molecule exhibiting rotation and vibration at a specific quantized energy level. The obtained spectrum of the molecule is influenced by the change in the permanent dipole moment of the molecule, which is attributed to the change in rotational and vibrational motion. The wavenumber range lies in the region of 400 to 4000 cm^{-1}. These spectra offer comprehensive insights into the nature of the atoms, stretching and bending vibration band, spatial orientation, and the chemical linkage forces between them. Nicolet iS5 THERMO Electron Scientific Instrument analyzed the functional group of the designed catalyst and solketal using a KBr pellet.

3.5.4 BET surface area

The textural properties of the synthesized catalyst, like specific surface area, pore volume, and pore diameter, were analyzed by using the N_2-adsorption-desorption isotherm. The

surface area of the catalyst was measured by Bruner, Emmet, and Teller (BET) theory at their boiling temperature. The importance of BET theory resides in its capacity to ascertain the number of molecules needed to build a monolayer on a solid surface, even though such a monolayer of adsorbed gas is not actually formed. The BET equation for calculating the surface area is given by

$$\frac{P}{V\,(P0-P)} = \frac{1}{Vm.C} + \left(\frac{C-1}{Vm.C}\right) \times \frac{P}{P0} \tag{3.2}$$

Where P = Equilibrium adsorption pressure (mmHg)

P_0 = Saturation vapor pressure of the adsorbent (mmHg)

V = Volume of gas adsorbed at pressure p (STP)

Vm = Volume of gas adsorbed for monolayer, ml (STP)

C = BET constant

Plotting a graph between P/V (P_0-P) and relative pressure (P/P_0) obtained a straight line with a slope of C-1/Vm.C and intercept of 1/Vm.C, respectively. Furthermore, the specific surface area of synthesized catalysts can be calculated using this equation,

$$\text{Surface area} = \frac{Vm.NA}{22141 \times wt.} \times A \tag{3.3}$$

Where, NA = Avogadro number (6.023×10^{23})

wt. = weight of catalyst (gm)

A = effective cross-sectional area of adsorbate molecule (for N_2 molecule = 16.2)

The surface area was assessed at the temperature of liquid nitrogen (-196 ^oC) using BELLSORP MAX II & BELCAT-II surface area analyzer. Before analysis, approx. 0.2 mg of catalyst sample were degassed for 6 h at 300 ^oC with nitrogen gas to eliminate any adsorbed impurities. Barret-Joyner-Halenda (BJH) method is also used to calculate the average pore volume along with the pore diameter.

3.5.5 SEM-EDX

SEM analysis is a destructive technique used to evaluate the surface topology, particle size, and various organic and inorganic substances on the catalyst surface. Scanning electron microscopy (SEM) provides a high-resolution image of the catalyst by redirecting an electron beam across the surface and capturing secondary or backscattered electron signals. The elemental constituents and quantitative compositional information were visualized by an energy-dispersive X-ray analysis (EDX or EDAX). These techniques can be quantitative, semi-quantitative, and qualitative and give detailed information about the spatial distribution of elements through elemental mapping. SEM provides the image at magnification up to ~ X50,000, enabling the sub-micron scale features to be seen, i.e., significantly smaller than those visible in the optical microscope field of view. The fabricated catalyst's elemental composition was detected by using EVO-Scanning Electron Microscope MA15/18 (CARL ZEISS MICROSCOPY LTD), which was equipped with the EDX detector (energy dispersive spectroscopy) unit by 51N1000-EDS system.

3.5.6. X-ray Photoelectron Spectroscopy (XPS)

The elemental composition, to a very small extent, empirical formula, and oxidation state of the elements catalyst can all be assessed by using X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy, for chemical analysis. It is a simple surface-sensitive phenomenon that informs about the surface chemistry of a catalyst. These spectra are created by irradiating the beam

of X-ray on a solid catalyst surface, and the emitted electron generates the kinetic energy from the uppermost 1 to 10 nm of the sample being analyzed. A standard XPS spectrum can depict the count of the detected electrons at a particular binding energy. A set of characteristics of XPS peaks originated from each element. The XPS analysis was conducted by using a K-Alpha spectrometer fitted with an aluminum (Al kα radiation)

monochromator source having energy 1486.7 eV operated at 15 kV and 20 mA. Taking C 1s peak (284.6 eV) as a reference to calibrate the all-binding energies of all elements.

3.5.7. NH_3-TPD analysis

The acidic amount on the catalyst surface was investigated by NH_3- temperature-programmed desorption (NH_3-TPD) equipped with a TCD detector. Firstly, the sample underwent degassing at 550 ^oC with a 10 ^oC/min heating rate for 1 h in the presence of He as a carrier gas. Subsequently, the reactor was cooled down to 100 ^oC, and the sample was then subjected to streams of 10 %- NH_3/He for 30 min. Following this, the sample was exposed to He at 100 ^oC for 1 h to eliminate the physically adsorbed ammonia. The desorbed ammonia was then continuously monitored using a temperature program with a heating rate of 10 ^oC/min. The catalyst acidity was detected through BELCAT II from MicrotracBEL Corp.

3.5.8. Acidity of catalyst by N-butylamine titration method

The acidity of the synthesized catalyst was also determined using the N-butylamine titration method, which used neutral red as an indicator. The presence of acidic sites and the acidity of the catalyst are pivotal factors in glycerol acetalization reactions. Consequently, it is imperative to investigate the acidic strength of the catalyst. Initially, the required amount of catalyst was submerged in the required amount of 0.05 M solution of N-butylamine in a toluene system and left to stir overnight at 30 ^oC. The solid catalyst was then separated from the reaction mixture. The filtrate was titrated against trichloroacetic acid in a toluene solution by adding two drops of neutral red as an indicator. The total acidity is represented in mmol g^{-1}.

3.6. Catalyst activity study

The glycerol acetalization reaction of solketal was carried out at atmospheric temperature and pressure in the range of 50-80 ^oC in a 100 ml round bottom flask fitted with a reflux

condenser. The whole setup is immersed in a silica oil bath fixed on a magnetic stirrer (Tarson digital spinout) to provide continuous heating and stirring. Initially, the required amount of glycerol and acetone was taken in a flask, followed by the addition of a certain amount of synthesized catalyst, which was allowed to stir at a specific temperature and time. After completion of the reaction, the product mixture was segregated from the mother liquor using centrifugation, and excess acetone was recovered using a rotatory evaporator. Then, the obtained product was quantitively and qualitatively analyzed by using gas chromatography-mass spectrometry, ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopy.

3.6.1. GC-MS analysis

Gas chromatography (Agilent technology 7890B) equipped with HP-5 with 30m × 0.32 mm × 0.25 micro m and fitted with a flame ionizer detector (FID) with a split injection mode was used for the quantitative analysis of the synthesized product. Initially, the oven temperature was fixed at 80 ^{o}C and then increased to 250 ^{o}C with an increasing rate of 20 ^{o}C/min. The injector temperature was fixed at 250 ^{o}C, whereas the detector was kept constant at 280 ^{o}C. 1,4-dioxane was taken as an internal standard for analysis of the synthesized product. The glycerol conversion, selectivity, and yield percentage of solketal were calculated using the following equation,

$$\text{Glycerol conversion (\%)} = \frac{initial\ moles\ of\ glycerol - remaining\ moles\ of\ glycerol}{initail\ moles\ of\ glycerol} \times 100 \quad (3.4)$$

$$\text{Solketal selectivity (\%)} = \frac{No.of\ moles\ of\ isolted\ solketal}{Total\ no.of\ moles\ of\ all\ product} \times 100 \quad (3.5)$$

$$\text{Solketal Yield (\%)} = \frac{\text{Glycerol conversion \%} \times \text{solketal selectivity \%}}{100} \quad (3.6)$$

3.6.2. ^{1}H NMR and ^{13}C NMR spectra

The NMR technique is also used for the analysis of the synthesized product. Proton NMR gives information about the presence of various types of protons signal for different types of protons in the product. Whereas the different type of carbon NMR signals signifies the presence of different environments of carbon moiety, confirming the solketal synthesis. NMR spectroscopy illustrates the structure of synthesized products. In this study, ^{1}H NMR along with ^{13}C NMR were attained by AVH D 500 AVANCE III HD 500 MHz OneBay NMR (Bruker). DMSO-d6 is used as an NMR solvent.