# Synthesis and Characterization of $SO_4^{2-}$ Loaded Mixed Oxides Heterogeneous Catalyst: Application in Bio-lubricants

*A*

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*Submitted By*

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UNDER THE SUPERVISION OF

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## CERTIFICATE

This is to certify that the thesis entitled **"Synthesis and Characterization of $SO_4^{2-}$ Loaded Mixed Oxides Heterogeneous Catalyst: Application in Bio-lubricants"** submitted by **Ms. Navneet Kaur** in the partial fulfillment of the requirements for the degree of **Master of Science in Chemistry** from **Thapar University, Patiala** is a bonafied piece of work carried out under the guidance and supervision of **Dr. Amjad Ali,** Associate Professor and Head, and **Dr. Soumen Basu**, Associate Professor, School of Chemistry and Biochemistry, Thapar University, Patiala and no part of this project has been submitted for award of any other degree in this or any other university.

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## SELF DECLARATION

The work embodied in the project entitled **"Synthesis and Characterization of $SO_4^{2-}$ Loaded Mixed Oxides Heterogeneous Catalyst: Application in Bio-lubricants"** has been done by me in the partial fulfillment of requirement for the award of degree of **Masters of Science in Chemistry,** submitted in the **School of Chemistry and Biochemistry, Thapar University, Patiala,** is an authentic record of my own carried out under the supervision and guidance of **Dr. Amjad Ali,** Associate Professor and Head, School Of Chemistry and Biochemistry and **Dr. Soumen Basu**, Associate Professor, Thapar University, Patiala. All the ideas and references have been duly acknowledged.

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## TABLE OF CONTENT

## ABSTRACT

A number of $SO_4^{2-}$ loaded mixed oxides heterogeneous catalysts were prepared by co-precipitation method and sol gel method and their catalytic activities were explored for esterification of fatty acids. The physico-chemical properties of the catalysts were evaluated by powder XRD, TGA, SEM-EDS and Mapping, FT-IR and FT-NMR studies. The prepared catalyst was successfully employed for the esterification of fatty acids. Out of the prepared catalysts, Si-Zr/$SO_4^{2-}$ catalyst has shown 97 % conversion of fatty acid into fatty acid methyl ester (FAME).Various techniques like $^{1}$H-NMR, $^{13}$C-NMR andFT-IR were employed to characterize the FAME obtained during the esterification reaction.

The optimized reaction conditions for esterification reaction are 7 wt% catalyst (with respect to Oleic acid), 65 ºC reaction temperature, 12:1 methanol to oleic acid molar ratio, and 2.5 hours of reaction duration.

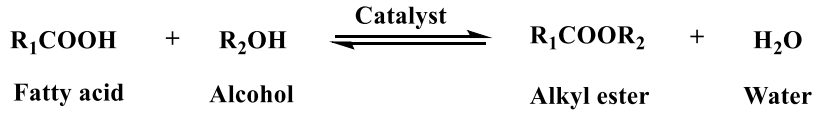
# CHAPTER 1

# INTRODUCTION AND LITRATURE REVIEW

## 1.1 INTRODUCTION

Lubrication of the engine fuel plays a vital role in prolonging the life of engine. The level of the lubricity determines the quality of different fuels. Good lubricity provides protection against wear and also reduces friction of locomotive parts (Tung *et al*., **2004)**. Lubricants are liquid products derived primarily from the petroleum distillation (Åkerman *et al*., **2011**). They have been produced on a large scale, worldwide due to their large number of applications in the fuel industry as machine oils, hydraulic oils, pump sets, insulating oils, compressor oils for generators etc. (Saboya *et al*., **2017**; Trivedi *et al*., **2015**). The rapid increase in the production of automobiles has led to greater demand of lubricants in the market. Earlier, mineral oils have been used for the production of lubricants due to their low price (Erhan *et al*., **2006**). Beside of their tremendous applications, main difficulties coming across in the use of conventional lubricants prepared from mineral oil are their poor biodegradability, toxicity (Fox *et al*., **2007**), and dependence on the non-renewable sources, which are depleting at faster rate (Willing *et al*., **2001**). Most of the conventional lubricants become pollutants worldwide due to the incidents like spillage, evaporation, and total loss lubrication (two-stroke engines, concrete mould release oils, exhaust fumes in engines) causing harmful or toxicological effects in the environment (Minami *et al*., **2017**). In order to lessen down the dependency on the non-renewable sources, developing fluid industries are putting more emphasis on finding the substitute for the mineral oil (Hill *et al*., **2000**). Thus there is a need of hour to develop a bio-based lubricant which will be non-toxic, biodegradable, environmental friendly, and increase the energy proficiency of the motorized sector (Singh *et al*., **2017**). Plant-based oils having long chain hydrocarbons have emerged as attractive raw materials to substitute the conventional mineral oils for the biodegradable lubricant production (Heikal *et al*., **2017**). Bio based lubricants will lessen down the environmental stress caused by petroleum based lubricants as they possess properties like higher flash point, lesser oil mist emission, and constant viscosity (Oh *et al*., **2013**). Synthetic bio lubricants can be prepared by two different pathways: 1) by the esterification of free fatty acids (FFAs) derived from vegetable oils with alcohols having a long (typically > C8) alkyl groups forming esters of $C_{12}$-$C_{36}$ lubricant range (Trivedi *et al*., **2015**) as shown in Scheme 1; 2) by direct transesterification of

vegetable oils (Oh *et al*., **2013**). In industry, the alkyl chain having length $C_{18}$-$C_{22}$ (oleic acid and erucic acid) have wide application as lubricant (Bart *et al*., **2013**). FFAs can be easily derived from the acid catalyzed hydrolysis of vegetable oils. Simple esters formed using small alcohol like methanol, ethanol, and propanol can be used in cosmetics, lubricants and in personal care products as emollients. However the higher esters like methyl palmitate, formed from methanol and palmitic acid can be used as an adhesive, ingredient in toilet soap, as a biodiesel, a solvent in paint industry (Yaakob *et al*., **2004**), in the production of detergents and cosmetics in the chemical industry (kiss *at al*., **2006**)




Scheme 1: Esterification of fatty acids with alcohol

Acid like oleic acid, stearic acid etc. has been used widely for the formation of fatty acid alkyl ester (FAAE). These fatty acids have bio based origin as they are the main constituent of vegetable oils such as soybean, sunflower, and rapeseed oil (Essamlali *et al*., **2017**). Earlier lubricant industry has been dominated by the use of homogeneous catalysts like $H_2SO_4$ due to their easy use and lesser reaction time. Although they provide higher conversions, their neutralization and separation from the mixture makes the task very tedious and time consuming. These limitations can be avoided by the use of heterogeneous catalysts that can eliminate the steps associated with separation and purification. But few of the heterogeneous catalyst possess lesser surface area, poor porosity and reusability. Presently, mesoporous catalysts have gained much attention as heterogeneous catalyst because of their characteristic properties, like larger surface area, mesoporous channels with flexible pore size and desirable thermal stability (Soltani *et al*., **2017**; Saravanan *et al*., **2016**). In present work various sulphated silica based heterogeneous acid catalysts have been studied for carrying out the esterification of different fatty acids with different alcohols, forming FAME which tend to be implemented globally for the production of biodegradable lubricants (Petran *et al*., **2008**).

## 1.2 LITERATURE REVIEW

Bio-lubricants are the oleo-chemical esters usually plant origin, prepared from esterification reaction of fatty acid with alcohol. Fatty acid alkyl ester (FAAE) is an environmentally friendly

fuel, produced either from fatty acids like oleic acid, palmitic acid, stearic acid or vegetable oils or animal fats. Generally, lubricants offer variety of services like prevention against wear and tear, rust and corrosion, maintaining viscosity at elevated temperature to allow engine to execute excellent. For enhancing utility of plant oils and fatty acids as lubricants, mainly their carboxylic group has been modified by esterification reaction. Fatty acid methyl esters (FAME) derived from vegetable oil by esterification reaction facilitates 20% decrease in friction when used in diesel fuel, enhance the lubricating properties of the fuel (Sulek *et al*., **2010**).

Esterification reaction could be carried out either by adopting catalytic or non-catalytic approach. In non-catalytic approach supercritical conditions have been opted for carrying out the reaction which makes it difficult to execute this approach at large scale (Coniglio *et al*., **2014**). On the other hand bio-catalysts involving some enzyme like lipase (Ghaly *et al*.,**2010**; Scillipoti *et al*., **2017**) and acidic catalysts have been used widely for carrying out the esterification reaction under optimized conditions (LAM *et al*., **2010**). Earlier homogenous catalysts like $H_2SO_4$, *p*-toluenesulfonic acid, or phosphoric acid have been employed for carrying out the esterification reaction for the production of esters. Non-reusability, corrosive nature, neutralization, separation from the reaction mixture and problems associated with their discharge have put a limit upon the use of homogeneous catalyst (Chongkhong *et al*., **2007**). These limitations of homogeneous catalyst can be overcome by the using ecofriendly heterogeneous acid catalyst (Lôbo *et al*., **2014**). These are non-corrosive in nature, have long catalyst lifetime, can be easily separated from the reaction mixture (Al-Jaberi *et al*., **2017**; Helwani *et al*., **2009**) can conduct esterification and transesterification reaction simultaneously.

Different types of short chain alcohol like methanol, ethanol, propanol, and butanol have been used in the esterification reaction (Bondioli *et al*., **2004**). Due to small side chain, easy availability, high reactivity, low-priced methanol is more frequently used for the esterification reaction as compared to other alcohols (Musa *et al*., **2014**). Moreover due to low density, FAME can be easily separated out from the reaction. The fact has been determined by the mesoporous Al-MCM-41 catalyzed esterification of palmitic acid with different alcohols. Among all, methanol was most reactive showing 79% conversion in 2h at 130 °C (Carmo *et al*., **2009**). Further $Nb_2O_5$ based esterification showed better conversion with methanol (82%) than ethanol. Moreover it has been found that the water produced in the reaction act as inhibitor for the

forward reaction as it facilitate hydrolysis of the ester produced during the reaction (Arandha *et al*., **2009**).

In literature, a large number of heterogeneous acid catalysts have been reported for carrying out the esterification reaction. A complex of organozinc with mono-aluminum substituted polyoxotungsten (TBA-P-Al-Zr) was employed as heterogeneous solid acid catalyst for esterification of linoleic acid with methanol under reaction conditions of alcohol to acid molar ratio of (176:1), catalyst amount (19.1μmol) at 82 °C for 6h. The yield of product is 83% (Kato *et al.*, **2017**). TDA modified 12-phosphotungstic acid was used for conducting esterification reaction of oleic acid with methanol. It has been found that TDA (1,2,3-trizaole-4,5-dicarboxylic acid (TDA) was incorporated into PTA (12-phosphotungstic acid) keeping its kegging structure intact. The prepared catalyst exhibit good water resistance and higher acidic strength. TDA make PTA less soluble in polar solvents enhancing its reusability (up to 6 cycles) showing 95.4% conversion (Wang *et al*., **2017**). Mesoporous sulphated Zr-KIT-6 has been used as heterogeneous catalyst for the esterification of oleic acid with methanol. A very high reaction conditions are employed for production of FAME upto ~96% yield (Gopinath *et al*., **2017**). Sulfonic acid modified hybrid mesoporous silica (SBA-15-$SO_3$H-P123) catalyzed esterification of palmitic acid yielded 92% methyl palmitate in 3h at 85 °C (Mbarka *et al*., **2003**). Catalytic activity of prepared catalyst was found comparable with the conc. $H_2SO_4$ (homogenous catalyst). Similarly, esterification reaction catalyzed by Si-Ti/$SO_4^{2-}$ at high alcohol to acid ratio furnished 93.8% FAME at 120 °C (Shao *et al*., **2013**). Mesoporous MCM-41 immobilized with silicotungstic acid (HSiW) has also been employed as a catalyst for the formation of fatty acid alkyl ester. The catalyst activity showed sharp decrease in second catalytic run (81.2% to 62.3%) in the second run. It has been found that HSiW species got partially eluted as it had weak electrostatic interactions with the -OH group on the surface of the support (Chen *et al*., **2016**).

Aerogel sulfonated $ZrO_2$-$SiO_2$ (AS-ZrSi) catalyst was prepared by sol gel method followed by supercritical drying (SCD). Esterification carried out by AS-ZrSi give 91% stearic ester, in 7h. The study revealed that SCD method improves acidic, structural and textural properties of the catalyst, which further improve the product yield (Saravanan *et al*., **2016**). Polymeric resins like Amberlyst have also been used as a heterogeneous catalyst for the esterification reaction. Out of Amberlyst-15 and Amberlyst BD-20, amberlyst-15 found to be more porous. On contrary Amberlyst BD-20 showed better conversion. It has been attributed to

the fact that more the porous structure more water will be adsorbed on the surface thus inhibits its catalytic activity after each run. On the other hand Amberlyst BD-20 does not have many pores so provide no opportunity for water to adsorb on the surface so its catalytic activity is maintained (Park *et al*., **2010**). Deep eutectic solvent (DES) has been employed for esterification of oleic acid using Amberlyst as a catalyst. It has been found that product formation increases with DES. DES-Amberlyst reduces the problem associated with water during esterification because these solvent have water absorbing functional groups. But overall effect of DES was more on Amberlyst BD20 than Amberlyst 15 because of their different structures (Pan *et al*., **2016**). Amberlyst 15 catalyst has also been employed for the synthesis of bio lubricants from oleic acid using ethanol (Hykkerud *et al*., **2016**). However, only 53% conversion was reported. Similarly other heterogeneous catalysts like $WO_3/ZrO_2$, sulphated zirconia, $SO_4^{2-}$/Fe-Al-$PO_4$ etc. have been employed for the esterification reactions as shown in Table 1.

**Table 1.** Different solid acid catalysts and their performances in FAME synthesis

| S. No. | Catalyst | Fatty acid | Alcohol | Temp. (˚C) | Al/Ac ratio | Catalyst amount (wt%) | Time (h) | FAME yield (%) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| **1.** | TDA-PTA | Linoleic acid | Methanol | 80 | 8:1 | 5 | 6 | 95.4 | Wang *et al*., **2017** |
| **2.** | $SO_4^{2-}$/Zr-KIT | Oleic acid | Methanol | 120 | 20:1 | 4 | 6 | 96 | Gopinath *et al*.,**2017** |
| **3.** | $SO_4^{2-}/Fe_x$-$Al_{1-x}PO_4$ | Caprylic acid | Ethanol | 75 | 6:1 | 1.5 | 4 | 92.4 | Liu *et al*., **2017** |
| **4.** | Al-MCM-41 | Palmitic acid | Methanol | 130 | 60:1 | 0.6 | 2 | 79 | Carmo *et al*., **2009** |
| **5.** | SBA-15-$SO_3$H-P123 | Palmitic acid | Methanol | 85 | 20:1 | 10 | 3 | 85 | Mbarka *et al*., **2003** |
| **6.** | $Nb_2O_5$ | Propionic acid | Methanol | 120 | 15:1 | 2 | 4 | 92 | Arandha *et al*., **2009** |
| **7.** | $SO_4^2/SnO_2$ | Oleic acid | Ethanol | 81.85 | 10:1 | 3 | 2.66 | 50 | Jose de silva *et al*., **2013** |
| **8.** | HSiW/MCM-41 | Oleic acid | Methanol | 80 | 2:1 | 25 | 10 | 81.2 | Chem *et al*., **2016** |
| **9.** | sulfonated $ZrO_2$-$SiO_2$ (AS-ZrSi) | Stearic acid | Methanol | 60 | 20:1 | 1.5 | 7 | 91 | Saravanan *et al*.,**2016** |
| **10.** | coal-based heterogeneous acid catalysts | Oleic acid | Methanol | 135 | 10:1 | 10 | 4 | 97 | Yu *et al*., **2016** |
| **11.** | Amberlyst 15 | Oleic acid | Methanol | 85 | 12:1 | 20 | 1.66 | >90 | Pan *et al*., **2016** |
| **12.** | Amberlyst 15 | Oleic acid | Ethanol | 60 | 1:1 | 20 | 6 | 53 | Hykkerud *et al*., **2016** |

**Al = Alcohol and Ac = Acid**

From the literature survey it is concluded that different catalyst were employed for esterification reactions, few of them have provided > 90% yield, but suffer from few shortcomings like poor reusability due to leaching of the catalyst and poor water resistance. Beside this high reaction temperature, high alcohol to acid ratio and longer reaction time is required for obtaining acceptable yield by using some catalysts.

# CHAPTER 2

# RESEARCH GAP AND OBJECTIVES

## 2.1 RESEARCH GAP

In literature reports, esterification process was carried out in presence of a variety of heterogeneous catalyst. However, most of the catalyst demand reaction temperature up to 135˚C (Gopinath et al., 2017; Carmo et al., 2009; and Yu et al., 2016) and high molar ratio of alcohol to acid (up to 60:1) (Carmo et al., 2009). However, even under these extreme reaction conditions only partial conversion levels were achieved. Thus, to improve the product yield under relatively mild reaction condition, development of new modified catalyst is essential.

## 2.2 OBJECTIVES

1. To prepare mixed metal oxide as heterogeneous solid catalyst by co-precipitation and sol-gel method.
2. To characterize the catalyst by physico-chemical techniques like powder XRD, FT-IR, TGA, SEM-EDS, NMR.
3. Application of the prepared catalyst for carrying out the esterification of different fatty acids employing various alcohols.

**CHAPTER 3**

**EXPERIMENTAL METHODS**

## 3. EXPERIMENTAL METHODS

### 3.1 MATERIALS

Fatty acids (Palmitic acid, Stearic acid, oleic acid), Titanium tetra chloride ($TiCl_4$), Aluminum chloride ($AlCl_3$), Silica gel for TLC, Ethyl acetate ($C_4H_8O_2$), and Acetic acid ($CH_3COOH$) from loba chemie. Zirconium oxychloride octahydrate ($ZrOCl_2.8H_2O$), Ethanol (EtOH), and Hexane ($C_6H_6$) from spectrochem Pvt. Ltd. Tetra ethyl ortho silicates (TEOS) from Aldrich, Amonium solution from EMPLURA, Methanol (MeOH) From RAMKEM were used directly without any further changes in them.

### 3.2 METHODS

#### 3.2.1 Powder X–ray diffraction (XRD)

Powder X-ray diffraction (XRD) patterns of synthesized catalysts were recorded by Panalytical's X'Pert Pro diffractometer operating at 40kV with nickel filtered monochromatic Cu Kα radiation (λ= 1.5406). The samples were scanned in the range of 2θ = 10 - 80° at the scanning speed of 2 min.

#### 3.2.2 Scanning Electron Microscopy (SEM)

To determine the structure and surface morphology of the catalysts were characterized by scanning electron microscopy (SEM) technique**.** SEM was performed on FESEM JEOL JSM 6510LV JAPAN. For analysis of the samples, firstly small amount of sample was sonicated in ethanol. Then, a drop of this suspension was placed on a sample holder by using carbon tape. Sample was then coated with gold and visualized with SEM instrument to see the morphology of particle.

#### 3.2.3 Thermo Gravimetric Analysis (TGA)

Thermal properties of sample were determined by thermogravimetric analysis. The measurements were carried out on a TGA 50 Shimadzu Corp 00568 in an inert atmosphere of nitrogen gas at a heating rate of 10 °C/min from 0° to 800 °C.

#### 3.2.4 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR was recorded on Perkin Elmer–Spectrum RX1 spectrophotometer in the range of 400-4000 $cm^{-1}$.

### 3.2.5 Fourier Transform Nuclear Magnetic Resonance (FT-NMR)

FT-NMR spectra of prepared FAME and free fatty acids were recorded on a JEOL ECS-400 (400 MHz) spectrophotometer. $CDCl_3$ is used as solvent during recording of all spectra and tetra methyl silane was used as an internal reference.

## 3.3 CATALYST PREPARATION

The mixed oxides were prepared by co-precipitation method and sol gel methods.

### 3.3.1 Preparation of $SiO_2$-$TiO_2/SO_4^{2-}$ and $SiO_2$-$ZrO_2/SO_4^{2-}$

Catalyst matrix ($Ti(OH)_4$-$Si(OH)_4$) has been prepared by dissolving 5 mL of titanium tetrachloride ($TiCl_4$) in 10 mL of water. Ammonia solution was added drop-wise to the above solution, until pH 10 was obtained and the mixture was stirred for 10 min. After 15 minutes, 10.48 mL of tetra ethyl orthosilicate (TEOS) was added slowly to the mixture with continuous stirring. The final suspension thus obtained was stirred for 1 h at 30 °C. Finally the suspension was filtered off, washed two or three times with deionized water to remove chloride ions, then dried at 120 °C for 24 h to obtain matrix material of $Si(OH)_4$- $Ti(OH)_4$.

To prepare the sulphated catalyst, 1g of the prepared catalyst matrix was suspended in 25 mL of deionized water and to this 1 M solution of sulphuric acid ($H_2SO_4$) was added. The above mixture was stirred at room temperature for 24 h, dried for 12 h at 120 °C and finally calcined for 5 h at 550 °C to obtain $SiO_2$-$TiO_2/SO_4^{2-}$.

Similarly $SiO_2$-$ZrO_2/SO_4^{2-}$ catalyst was also prepared by employing zirconium oxy chloride octahydrate ($ZrOCl_2.8H_2O$) as precursor in place of $TiCl_4$, but maintaining other reaction condition as described for the preparation of $SiO_2$-$TiO_2/SO_4^{2-}$.

### 3.3.2 Preparation of silica ($SiO_2$) Monolith by sol-gel method

For silica monolith formation, 1.1g of PEG (Poly ethylene glycol, 35000 series) was mixed in 16.5 mL of water and to this 30% of $HNO_3$ was added followed by the addition of 16.20 mL TEOS to obtain an emulsion. The resulted mixture was stirred at room temperature, until a clear solution was obtained. After that, 2.76 g of CTAB ($C_{16}$) was added slowly to avoid the formation of lump with continuous stirring at room temperature till the clear solution was obtained. The

resulting solution was filled in micro plates, covered with paraffin to avoid oxidation and is placed in oven for 3-4 days at 40 °C. The silica pellets thus obtained was poured into ammonia solution and obtained monoliths were dried in oven at 90 °C for 9 h. Monoliths were cooled at room temperature, washed with 0.1 M $HNO_3$ acid and finally with water, again dried at 40 °C for 4 days and finally calcined at 550 °C.

### 3.3.3 Preparation of $SiO_2$-$Al_2O_3/SO_4^{2-}$

For the preparation of $SiO_2$-$Al_2O_3/SO_4^{2-}$ catalyst, 1 g of prepared mesoporous silica monolith was suspended in 30 mL water and to this aqueous solution of $AlCl_3$ (0.27 g dissolved in 10 mL water) added dropwise. The resulted mixture was stirred for 24 h and then dried in oven for 24 h. To prepare sulphated catalyst, 1g of above alumina silica (powder) was suspended in 10 mL of water and to this 1 M sulphuric acid solution ($H_2SO_4$) was poured drop wise. The resulted mixture was stirred for 24 h, dried and finally calcined at 550 °C for 5 h.

## 3.4 ESTERIFICATION OF FATTY ACIDS

Esterification reactions were carried out in 50 mL double neck round bottom (RB) flask equipped with water cooled reflux condenser, magnetic stirrer, oil bath and thermometer. In a typical esterification reaction, 5 g of fatty acid was mixed with desired molar concentration of methanol and the catalyst in round bottom flask and was stirred (550 rpm) at 65 °C. In order to monitor the progress of reaction, the samples were withdrawn from the reaction mixture after every 15 min with the help of dropper and were subjected to thin layer chromatography (TLC). TLC was developed using hexane/ethyl acetate (95:5, v/v) as mobile phase, and silica gel as stationary phase as shown in Figure 1. The fatty acid methyl ester (FAME) were characterized by FT-IR, $^{1}H$ NMR and $^{13}C$ NMR techniques.

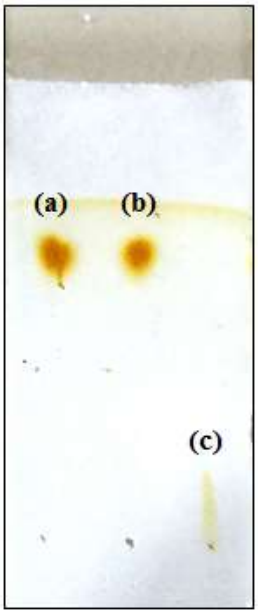



**Figure 1.** TLC analysis of (a) methyl oleate standard (Rf = 0.7), (b) fatty acid derived FAME (Rf = 0.7)

Formation of FAME was confirmed by comparing $R_f$ value (Retention Factor) of ester with standard Methyl oleate ($C_{19}H_{32}O_2$) (Figure.1). Prepared FAME (Fatty acid methyl ester) was quantified by $^1$H NMR using following equation (Knothe, **2001**).

$$\% \text{ FAME yeild} = \frac{2I \text{ (methoxy)}}{3I \text{ (methylene)}} \times 100$$

where $I_a$ and $I_b$ are the integrated peak areas of the methoxy and α-methylene protons at 3.6 and 2.3 ppm respectively.

## CHAPTER 4

## RESULTS AND DISCUSSION

### 4.1 CATALYST CHARACTERIZATION

#### 4.1.1 SEM-EDS and Mapping

Shape, size and morphology of the different bare and sulphate impregnated catalyst ($Si(OH)_4$-$Ti(OH)_4$, Si-Ti/$SO_4^{2-}$, $Si(OH)_4$-$Zr(OH)_4$ and Si-Zr/$SO_4^{2-}$) were characterized by SEM technique as shown in Figure 2. The SEM images of $Si(OH)_4$- $Ti(OH)_4$, and $Si(OH)_4$- $Zr(OH)_4$ showed particles in clusters with irregular geometry. The cluster formation in these could be due to the agglomeration of particles during their preparation. Upon sulphate impregnation, resulted in the formation of flakes or leaves shaped geometry Figure 2c and shape similar to water mosses Figure 2f in Si-Zr/$SO_4^{2-}$ and Si-Ti/$SO_4^{2-}$ catalyst, respectively. Elemental mapping images of $Si(OH)_4$- $Zr(OH)_4$, Si-Zr/$SO_4^{2-}$ and $Si(OH)_4$- $Ti(OH)_4$ and Si-Ti/$SO_4^{2-}$ **are shown in Appendix-1**. The elemental mapping supports the homogeneous distribution of all elements over the catalyst support.

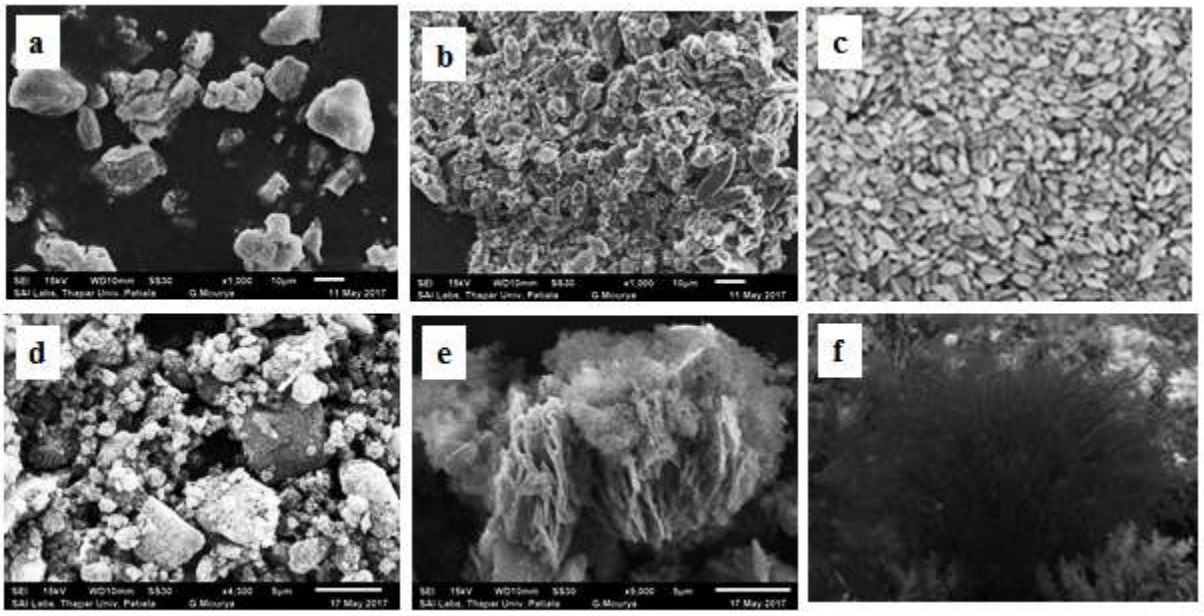



**Figure 2.** SEM image of (a) $Si(OH)_4$- $Zr(OH)_4$ (b) Si-Zr/$SO_4^{2-}$ (c) Flakes or leaf pettle (d) $Si(OH)_4$- $Ti(OH)_4$ (e) Si-Ti/$SO_4^{2-}$ (f) Water moss plant

EDS analyses of Si-Zr/$SO_4^{2-}$ and Si-Ti/$SO_4^{2-}$ showed 14.74 wt% and 4.77 wt% sulphur content, respectively, as shown in Table 2.

**Table 2:** EDS data of $Si(OH)_4$- $Zr(OH)_4$, Si-Zr/$SO_4^{2-}$ **,** $Si(OH)_4$- $Ti(OH)_4$ and Si-Ti/$SO_4^{2-}$

| Catalyst | Elements | | | | |
|---|---|---|---|---|---|
| | O (Wt %) | Si (Wt %) | Zr (Wt %) | Ti (Wt%) | S (Wt %) |
| $Si(OH)_4$- $Zr(OH)_4$ | 59.43 | 11.88 | 28.70 | - | - |
| Si-Zr/$SO_4^{2-}$ | 50.32 | 4.58 | 30.41 | - | 14.74 |
| $Si(OH)_4$- $Ti(OH)_4$ | 62.55 | 20.87 | - | 16.58 | - |
| Si-Ti/$SO_4^{2-}$ | 58.23 | 13.55 | - | 23.45 | 4.77 |

### 4.1.2 TGA Analysis

The $Si(OH)_4$-$Zr(OH)_4$and Si-Zr/$SO_4^{2-}$ were evaluated by mean of thermo gravimetric analysis. From Figure 3 indicated that thermal decomposition curve exhibit one and two weight loses stages for $Si(OH)_4$- $Zr(OH)_4$ and Si-Zr/$SO_4^{2-}$ respectively (El-Naggar *et al*., 2013). The first weight loss is observed in the region 100-180˚C for both the curves corresponding to the dehydration or water evaporation in both the curves in Figure 3a and Figure 3b. The second weight loss is observed in Si-Zr/$SO_4^{2-}$ above 600˚ C due to thermal decomposition of sulphate group as shown in Figure 3b (Dong *et al*., 2013).

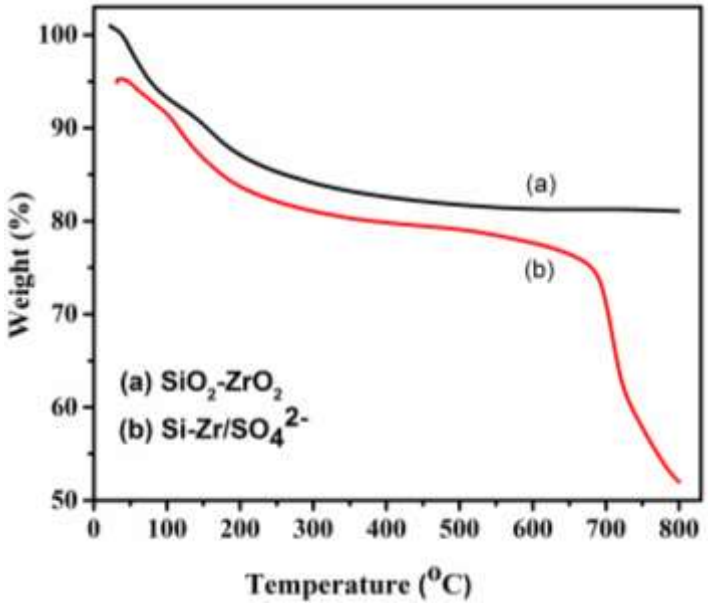



**Figure 3.** Thermo gravimetric analysis of (a) $Si(OH)_4$- $Zr(OH)_4$ and (b) Si-Zr/$SO_4^{2-}$

### 4.1.3 XRD Analysis

The powder XRD study of different supports ($Si(OH)_4$-$Al(OH)_3$, $Si(OH)_4$- $Ti(OH)_4$, and $Si(OH)_4$- $Zr(OH)_4$) and sulphate impregnated (Si-Al/$SO_4^{2-}$ , Si-Ti/$SO_4^{2-}$ and Si-Zr/$SO_4^{2-}$) catalyst have been performed and comparison of respective diffraction patterns is given in Figure 4. Presence of a broad peak at 2θ = 20-30 in the XRD patterns of supports Figure 4a ($Si(OH)_4$-$Al(OH)_3$) Figure 6c $Si(OH)_4$- $Ti(OH)_4$) and Figure 4e $Si(OH)_4$- $Zr(OH)_4$ indicates its poor crystalline nature. However sulphate impregnation over the prepared supports showed weak diffraction pattern in Figure 4b Si-Al/$SO_4^2$ and Figure 4d Si-Ti/$SO_4^{2-}$ corresponding to aluminium silicon oxide (JCPDS card no. 00-002-1160), aluminium sulphate (JCPDS card no. 00-001-0566), orthorhombic titanium dioxide (JCPDS code no. 03-065-2448), titanium oxide sulphate (JCPDS card no. 00-040-0653) and orthorhombic crystalline shape of sulphur dioxide (JCPDS card no. 01-073-2096). A large no. of new diffraction peaks in Figure 4f support the formation of zirconium silicate (JCPDS card no. 01-081-0590) and orthorhombic phase of zirconium sulphate (JCPDS card no. 00-024-1492) which are the source of acid sites in sulphated silica zirconia (Chen *et al*., 2007).

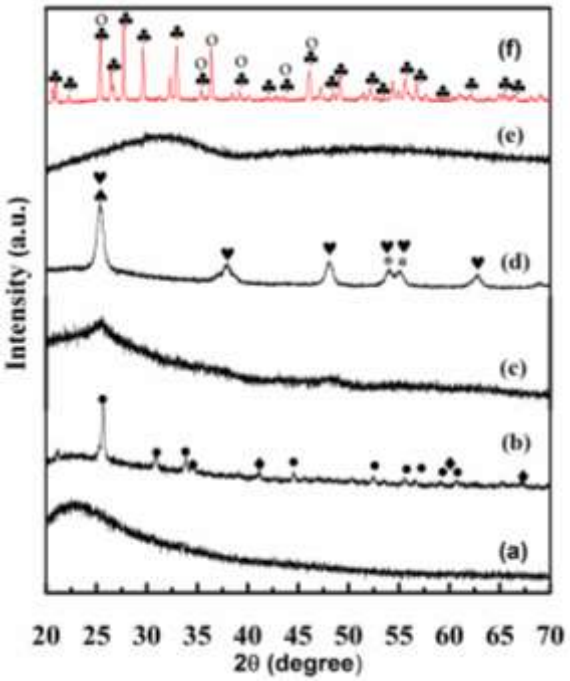



**Figure 4.** Comparative XRD pattern of different catalyst with or without sulphate loading (a) $Si(OH)_4$-$Al(OH)_3$ (b) Si-Al/$SO_4^{2-}$ (c) $Si(OH)_4$- $Ti(OH)_4$ (d) Si-Ti/$SO_4^{2-}$(e) $Si(OH)_4$- $Zr(OH)_4$ (f)

Si-Zr/$SO_4^{2-}$ (●=Aluminium sulphate peak), (♦=Aluminium silicon oxide), (♠=Sulphur dioxide), (♣=Zirconium sulphate), (○=Zirconium silicate), (♥=Titanium dioxide), (* = Titanium oxide sulphate)

### 4.1.4 FT-IR Analysis

The prepared catalysts were characterized by FT-IR to support the impregnation of sulphate over different supports as shown in Figure 5. The peak at 800 $cm^{-1}$ and 1100 $cm^{-1}$ is attributed to the symmetric and asymmetric vibrations, respectively, of Si—O in siloxane (Si—O—Si). The FT-IR spectra of the sulphated catalyst show a peak at 1200– 1100 $cm^{-1}$ which can be assigned to the S=O group (Ghoreishi *et al*., 2014; Shao *et al*., 2013)**.** Peaks observed at 600–700 $cm^{-1}$ due to S–O stretching as shown in Figure 5d and 5f confirmed the presence of sulfonic acid sites on silica zirconia and silica alumina supports. Peaks in the range of 1120–1230 $cm^{-1}$ are because of O═S═O stretching modes (Shah *et al*., 2014). O-H stretching peaks and scissor bending vibration appeared as a broad band at 3300- 3500 $cm^{-1}$ and at about 1635 $cm^{-1}$. A peak at 1200 $cm^{-1}$ is due to sulphated zirconium, this peak was absent in pure zirconium (D'Souza *et al*., 2006).

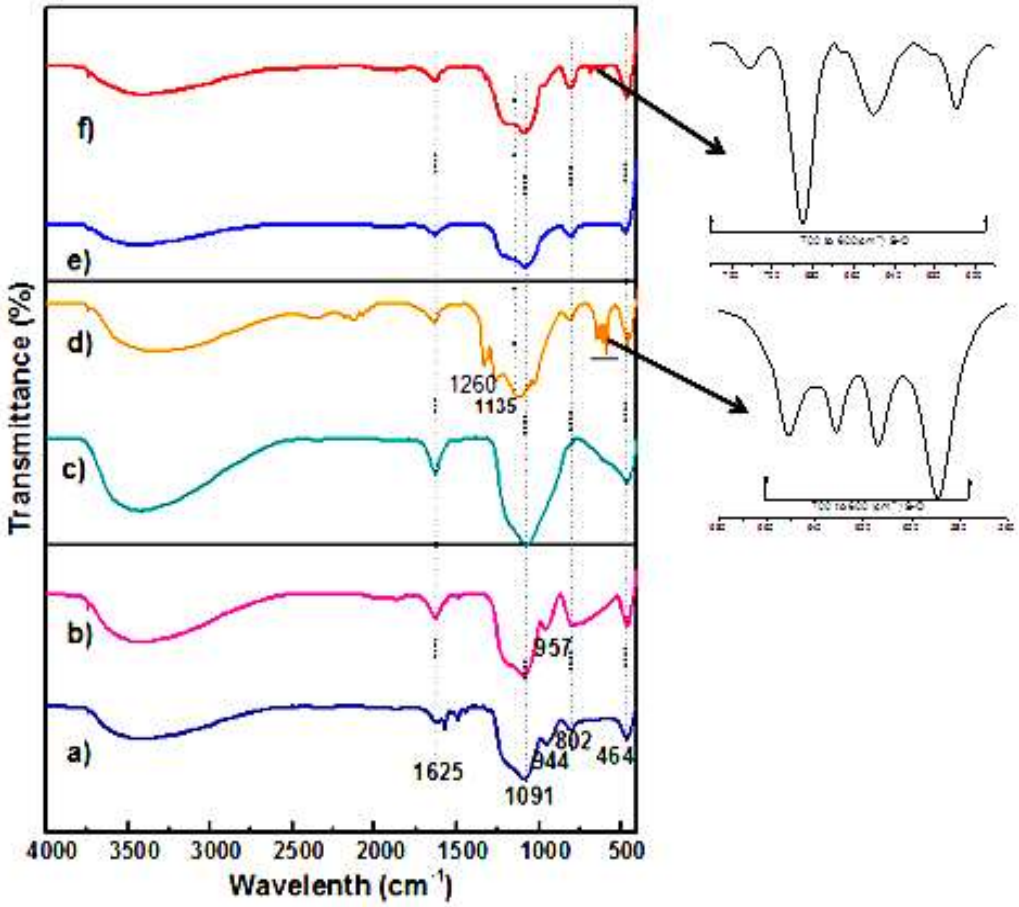



**Figure 5.** FT-IR transmittance spectra of sulphated and without sulphated catalyst (a) IR spectra of $Si(OH)_4$- $Ti(OH)_4$ (b) IR spectra of Si-Ti/$SO_4^{2-}$ (c)IR spectra of $Si(OH)_4$- $Zr(OH)_4$ (d) IR spectra of Si-Zr/$SO_4^{2-}$ (e) IR spectra of $Si(OH)_4$-$Al(OH)_3$ (f) IR spectra of Si-Al/$SO_4^{2-}$

FT-IR spectrum of Figure 5a ($Si(OH)_4$- $Ti(OH)_4$) and Figure 5b (Si-Ti/$SO_4^{2-}$) showed that all the peaks are same except a small shift in the peak from 944 $cm^{-1}$ to 957 $cm^{-1}$ in Figure 5b. This was assigned to be a combination of the stretching modes of the Si-O species in Si-OH groups and in Si-O-$Ti^{4+}$ sequences involving tetrahedrally coordinated $Ti^{4+}$ ions. (Han *et* al. 2001). Absence of peaks in between 600-700 $cm^{-1}$ in Figure 7b may be attributed to the absence of sulphonic acid sites.

### 4.2 FAME CHARACTERIZATION BY $^{1}$H NMR and $^{13}$C-NMR

Proton NMR technique is used for characterization and quantitative analysis of methyl oleate because this method is not only simple, fast and non-destructive but also did not require any

derivatization step.[1]H NMR spectra of oleic acid and its ester, methyl oleate, (FAME) is shown in Figure 6. Peaks observed at 5.25 and at 2.3 ppm in both the molecules correspond to the unsaturated protons and α-$CH_2$ protons respectively. In [1]H NMR spectra of methyl oleate, peak corresponding to –$OCH_3$ protons is observed at 3.6 ppm which support the formation of methyl oleate upon esterification of oleic acid with methanol as shown in Figure 6b.

[13]C-NMR spectra of oleic acid, (Figure 7) the peak corresponding to carbonyl group of oleic acid appeared at 180 ppm. Unsaturated and α $CH_2$ carbon peaks were observed at 130 and 30-40 ppm. The peak corresponding to –$OCH_3$ is observed at 51.4 ppm in Figure 7b supporting the formation of methyl oleate. Also carbonyl group peak shifted from 180 ppm in Figure 7a to 175 ppm in methyl oleate Figure 7b.

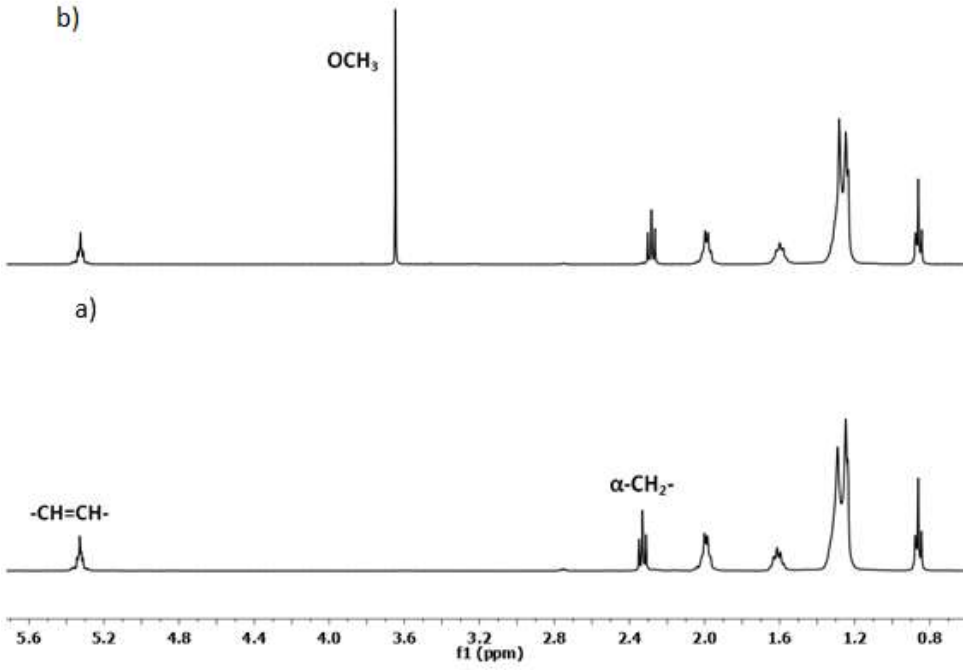



**Figure 6.** Comparison of [1]H NMR spectra of (a) Oleic acid (b) Methyl oleate

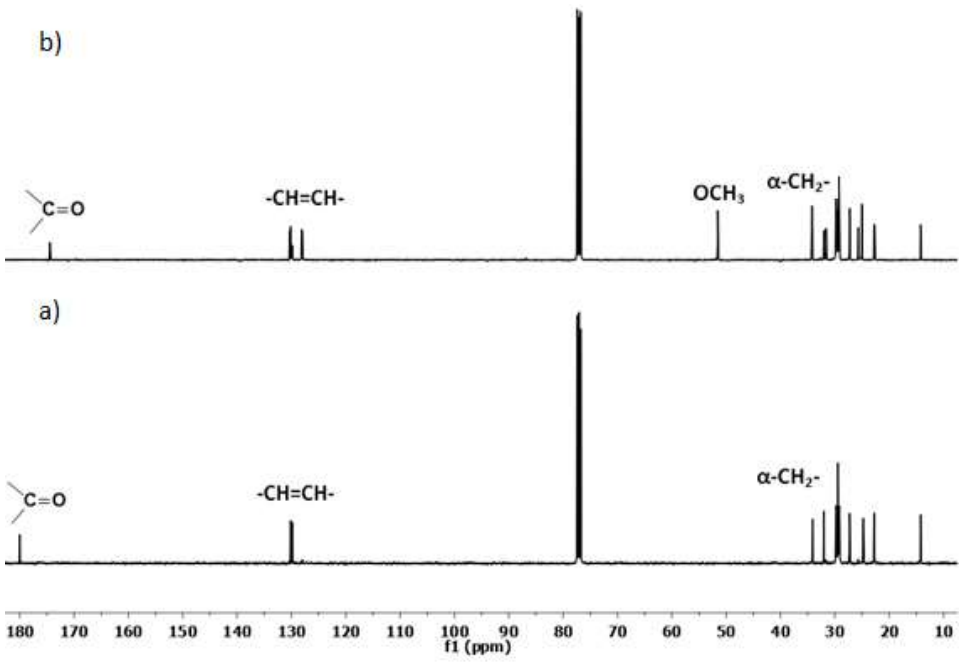



**Figure 7.** Comparison of $^{13}$C-NMR spectra of (a) Oleic acid (b) Methyl oleate

### 4.3 FAME CHARACTERIZATION BY FT-IR

FTIR spectra of oleic acid shows bands at 1285 and 1700 $cm^{-1}$ due to carboxylic C-OH and C=O vibrational frequencies as shown in Figure 8a. Upon esterification, there is shifting of the band frequencies from 1285 to 1192 $cm^{-1}$ and from 1750 $cm^{-1}$ to 1700 $cm^{-1}$ supporting the formation of ester group Figure 8b. Similar shifts are observed in case of stearic acid ester shown in Figure 8d.

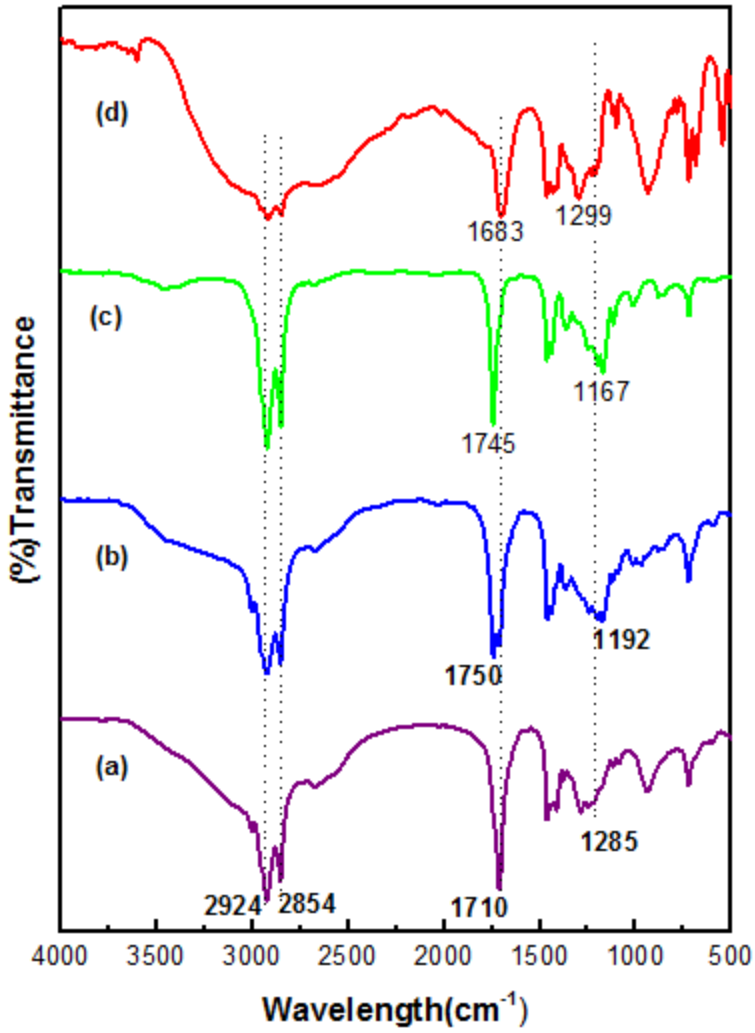



**Figure 8.** Depicts the FT-IR transmittance spectra of (a) Oleic acid (b) Methyl Oleate (c) Stearic acid (d) Methyl Stearate

### 4.4 CATALYTIC ACTIVITY

A screening of different catalysts was performed under similar reaction conditions (reaction temp.65˚C, 7 wt% catalyst, alcohol to acid molar ratio 12:1) to find the most promising heterogeneous acid catalyst for the esterification reaction. Among the various sulphated catalyst (Si-Ti/$SO_4^{2-}$, Si-Zr/$SO_4^{2-}$, Si-Al/$SO_4^{2-}$) Si-Zr/$SO_4^{2-}$ was found to be the best catalyst because it gives maximum yield. The experimental results are given in Table 3.From this table it is clear that bare silica support showed almost negligible activity with no conversion at all. However impregnation of sulphate upon silica enhances its catalytic activity of the prepared catalyst. None of the prepared catalyst showed any activity towards palmitic acid. For optimal catalytic activity,

the different reaction parameters like methanol to oleic acid ratio, catalyst weight % with respect to fatty acid, were optimized.

For optimal catalytic activity, the different reaction conditions were optimize. Esterification reaction has been carried out at a stirring speed of 550 rpm by changing one parameter at a time. These parameters are : Effect of different fatty acid with different catalyst, Effect of methanol to oleic acid ratio, Effect of catalyst weight %.

**Table 3:** Catalytic Activities of Different Catalysts with different acids

| Catalyst | Substrate | Catalyst amount (%) | Temp. ($^{o}$C) | Methanol/Acid Ratio | Time (h) | Yield (%) | Reusability |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | Oleic acid | 7 | 65 | 12:1 | 24 | NA | - |
| $SiO_2/SO_4^{2-}$ | Oleic acid | 7 | 65 | 12:1 | 10 | 7.2 | - |
| $SiO_2$-$TiO_2/SO_4^{2-}$ | Oleic acid | 5 | 65 | 12:1 | 2.20 | 55 | - |
| $SiO_2$-$TiO_2/SO_4^{2-}$ | Oleic acid | 7 | 65 | 12:1 | 1.45 | 60 | |
| $SiO_2$-$TiO_2/SO_4^{2-}$ | Oleic acid | 9 | 65 | 12:1 | 1.45 | 57 | - |
| $SiO_2$-$TiO_2/SO_4^{2-}$ | Palmitic acid | 7 | 65 | 12:1 | 24 | NA | - |
| $SiO_2$-$TiO_2/SO_4^{2-}$ | Acetic acid | 7 | 65 | 12:1 | 10 | 14 | - |
| $SiO_2$-$TiO_2/SO_4^{2-}$ | Stearic acid | 7 | 65 | 20:1 | 3 | 93.45 | - |
| $SiO_2$-$ZrO_2/SO_4^{2-}$ | Oleic acid | 7 | 65 | 12:1 | 2.25 | 97 | 4 |
| $SiO_2$-$ZrO_2/SO_4^{2-}$ | Palmitic acid | 7 | 65 | 20:1 | 24 | NA | - |
| $SiO_2$-$ZrO_2/SO_4^{2-}$ | Stearic acid | 7 | 65 | 20:1 | 10 | 94 | - |
| $SiO_2$-$ZrO_2/SO_4^{2-}$ | Acetic acid | 7 | 65 | 12:1 | 24 | NA | - |
| $SiO_2$-$ZrO_2/SO_4^{2-}$ | Propanoic acid | 7 | 65 | 12:1 | 24 | NA | - |
| $SiO_2$-$ZrO_2/SO_4^{2-}$ | valeric acid | 7 | 65 | 12:1 | 24 | NA | - |
| $SiO_2$-$Al_2O_3/SO_4^{2-}$ | Oleic acid | 7 | 65 | 12:1 | 6 | 73 | - |
| $SiO_2$-$Al_2O_3/SO_4^{2-}$ | Palmitic acid | 7 | 65 | 20:1 | 24 | NA | - |
| $SiO_2$-$Al_2O_3/SO_4^{2-}$ | Stearic acid | 7 | 65 | 20:1 | - | 10 | - |

### 4.4.1 Effect of different fatty acids with different catalyst

A series of esterification reaction has been carried out by using three different fatty acids such as oleic acid, stearic acid and palmitic acid with the prepared catalysts.

In particular Si-Zr/$SO_4^{2-}$ exhibit superior activity giving a conversion of 97% with oleic acid at 65 $^{o}$C for 2.25 h, probably because of the presence of large number of strong acid sites on the surface of catalyst. On the basis of above results, Si-Zr/$SO_4^{2-}$ showed potential to be used as a heterogeneous acid catalyst for esterification reactions (Figure 9).

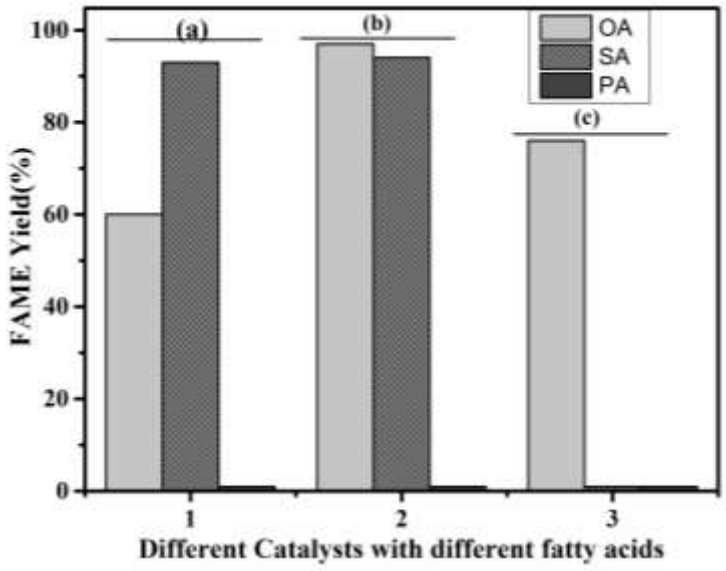



**Figure 9.** Depict the FAME yield using different fatty acid with different catalyst (a) Si-Ti/$SO_4^{2-}$, (b) Si-Zr/$SO_4^{2-}$, (c) Si-Al/$SO_4^{2-}$

### 4.4.2 Effect of methanol to oleic acid ratio

The effect of methanol to oleic acid ratio on esterification reaction is very important parameter which affects the FAME yield. The theoretical methanol to fatty acid molar ratio should be 1:1 for complete conversion of fatty acid to FAME. However esterification being a reversible reaction generally is carried out with excess of methanol to obtain maximum yield. To determine the optimal methanol /oleic acid molar ratio for Si-Zr/$SO_4^{2-}$ catalyst, the reactions were performed by changing methanol/oleic acid molar ratio from 6:1 to 18:1 for 2.25 h at 65 °C. It has been observed that the FAME yield increases from 45 to 97% with increase in the molar ratio from 6:1 to 12:1.but on further increase in the molar ratio has no significant influence on FAME yield as shown in Figure10.

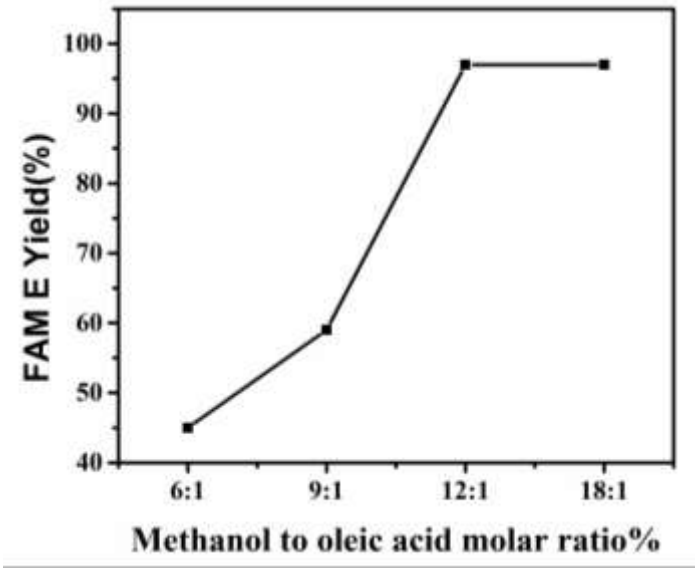



**Figure 10.** Effect of methanol to oleic acid molar ratio on FAME yield (reaction condition: catalyst amount 7 wt% with respect to oleic acid ;temperature 65 °C; and reaction duration, 2.5 h).

### 4.4.3 Effect of the catalyst amount

The amount of catalyst used in a chemical reaction has a significant effect on the production cost of any product. In general, the rate of reaction increases directly with increase in catalyst concentration because, number of active sites on the catalyst surface increases. However minimum amount of catalyst is preferable to make any process economically viable. So to determine the optimal concentration of catalyst, a series of esterification reaction of oleic acid with methanol to oleic acid molar ratio 12:1 were performed in the presence of 5 to 9 weight % (with respect to oleic acid) of Si-Zr/$SO_4^{2-}$ for 2.5 hours. The FAME yield increases with the increase in the amount of catalyst from 5 to 7wt % but on further increase in the FAME yield is observed at higher concentration of the catalyst (Figure11).

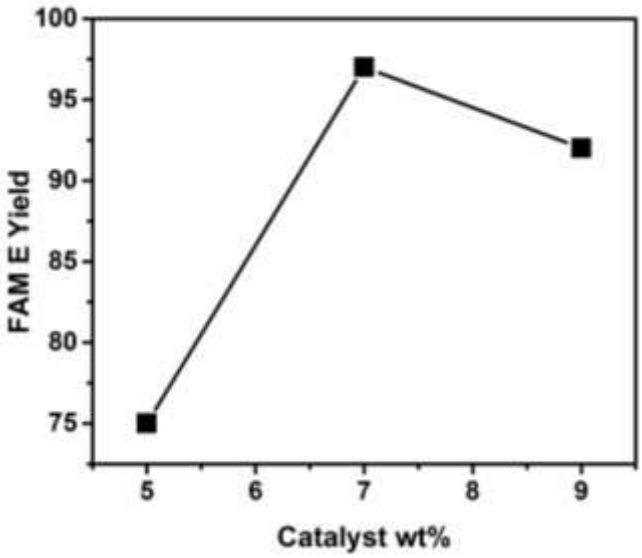



**Figure 11.** Effect of catalyst amount with respect to oleic acid on FAME yield (reaction conditions: methanol/oleic acid molar ratio, 12:1; temperature 65 °C; and reaction duration 2.5 h)

### 4.5 REUSABILITY STUDY

The reusability is an important property of heterogeneous catalysts over the homogeneous catalyst because it decreases the overall production cost of the reaction. To test the reusability of Si-Zr/$SO_4^{2-}$ catalyst, esterification of oleic acid was carried out with methanol under optimized reaction conditions. The catalyst was recovered by filtration after each catalytic run. The recovered catalyst was washed with hexane, dried at 120 °C and finally calcined at 550 °C. The catalyst thus regenerated was used for 3 successive catalytic cycles under the same experimental and regeneration methods. The partial loss of activity is observed in every succeeding run, this could be attributed to the leaching of active species ($SO_4^{2-}$) from the surface of catalyst. (Figure12)

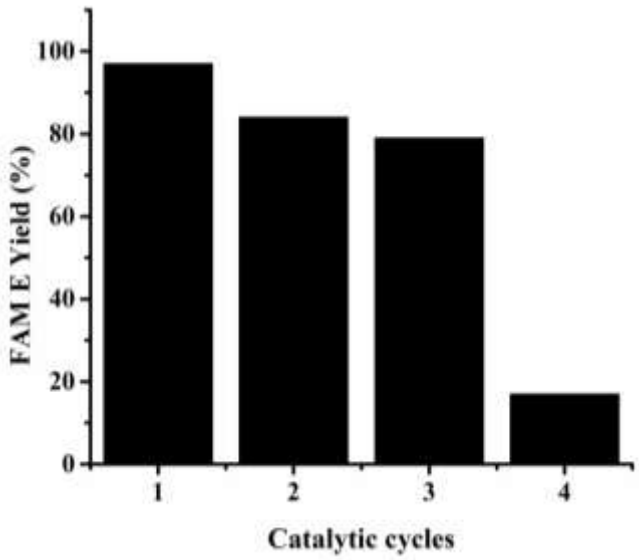



**Figure 12.** Reusability study of Si-Zr/$SO_4^{2-}$ catalyst esterification of oleic acid (reaction conditions: methanol/oleic acid molar ratio 12:1; catalyst amount, 7 wt % with respect to oleic acid; temperature, 65 °C; and reaction time 2.5 h)

### 4.5.1 XRD of reusable catalyst

The comparison of the XRD patterns (Figure 13) of fresh and reused catalyst shows some structural variations in reused catalyst. Appearance of peaks at 2θ = 28.3° in the diffraction pattern of reused catalyst supported the formation of cubic zirconium oxide sulfide as one of the major phase (JCPDS card number 01-087-2314). As can be seen in Table 5, the decrease in acidic strength may be responsible for the decline in (Zr-Si/$SO_4^{2-}$) the catalytic activity. At 2θ-(30.2, 50.2, and 35.0) peaks are due to tetragonal phase of zirconium silica (JCPDS card number 00-003-0630).Cubic phase of zirconium oxide (JCPDS card number 00-049-1642) and tetragonal phase of silica oxide (JCPDS card number 01-088-2486) formation appears in the diffraction pattern of reused catalyst. As seen from the diffraction pattern that zirconium sulphate peaks are absent in reused catalyst which is the main source of acidic sites in Si-Zr/$SO_4^{2-}$ (Chen *et al*., 2007).

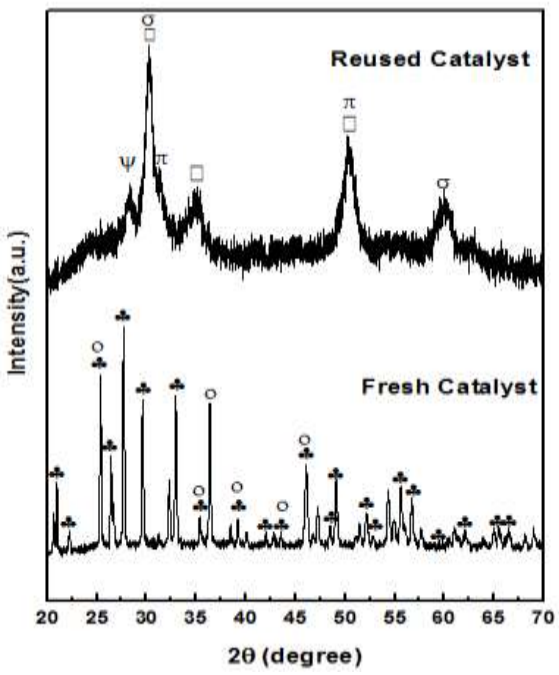



**Figure 13**. Comparative XRD pattern of Fresh and Reused catalyst (♣=Zirconium sulphate), (○=Zirconium silicate), (σ=Silica oxide), (π=Zirconium oxide), (ψ=Zirconium oxide sulfide), (□=Zirconium silicate).

### 4.5.2 SEM-EDS and Mapping of reused catalyst

Figure 14 show SEM images of fresh 14a and reused catalyst 14b. As seen from Figure the morphology of fresh catalyst is changed upon repeated use. The reused catalyst acquires irregular needle shaped geometry.

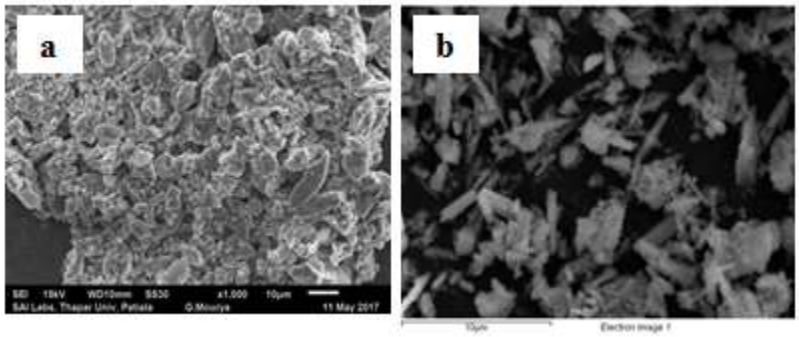



**Figure 14.** Show SEM images of Si-Zr/$SO_4^{2-}$ (a) Fresh and (b) Reused catalyst

The comparison of EDS data of fresh and reused catalyst is shown in Table 4. From the table it is clear that on repeated use the sulphur content is decreases from 14.74 % to 5.45 % to indicate the leaching of the sulphate species from the catalyst upon repeated use. The colour mapping images of fresh and reused catalyst is given in appendix 2.

**Table 4:** EDS data of fresh and reused catalyst (Si-Zr/$SO_4^{2-}$)

| Catalyst | Elements | | | |
|---|---|---|---|---|
| | **O (wt %)** | **Si (wt %)** | **Zr (wt %)** | **S (wt %)** |
| Fresh | 50.32 | 4.58 | 30.41 | 14.74 |
| Reused | 52.52 | 6.57 | 35.45 | 5.45 |

### 4.6 KINETICS

To study the kinetics of esterification reaction, the samples were taken out from the reaction mixture after every 30 minutes and were subjected to $^1$H NMR analysis to quantify the FAME yield. The conversion of oleic acid at different reaction duration was obtained and fitted in zero order (equation 1), first order (equation 2), and second order (equation 3) kinetic models,

$$\frac{Kt}{100} = X_{me} \quad \text{..... (1)}$$

$$\ln(1 - X_{me}) = kt \quad \text{..... (2)}$$

$$100kt = \frac{X_{me}}{1 - X_{me}} \quad \text{..... (3)}$$

where k is rate constant ($min^-$),

$M_e$ is the conversion of oleic acid to FAMEs at time t. The FAME yield obtained at various time intervals were fitted in equations 1, 2 and 3 and the corresponding plots are shown in Figure15. A linear fitting was obtained when equation 2 was followed to support that reaction has followed the pseudo first order kinetics, with the rate constant value of 0.022 $min^{-1}$ at 65° C.

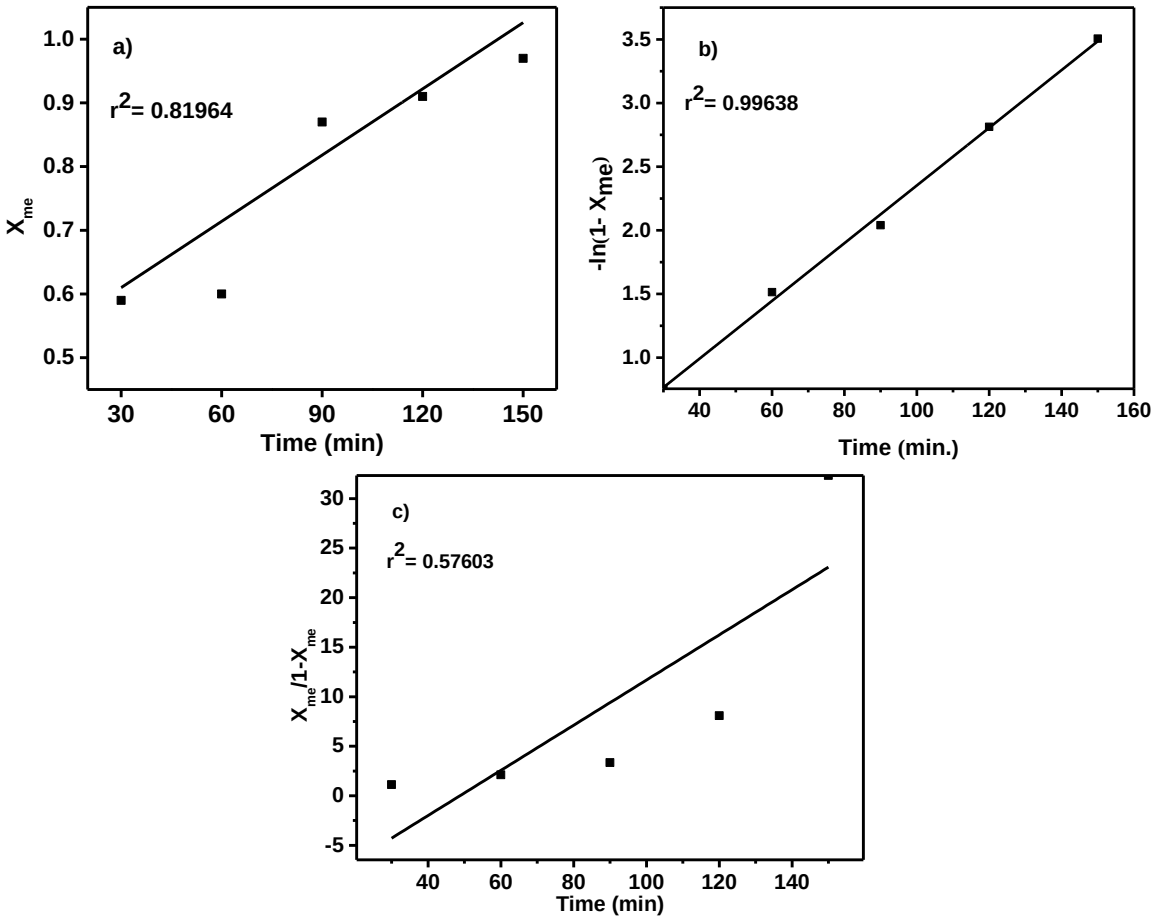



**Figure 15.** Plots of (a) Zero order reaction ($X_{me}$ versus time), (b) 1st order reaction (-ln(1-$X_{me}$)versus time) and (c) 2nd order reaction ($X_{me}/1-X_{me}$ versus time). [reaction conditions: methanol/Oleic acid molar ratio-12:1, catalyst amount- 7wt% with respect to acid and temperature 65°C]

## CHAPTER 5

## CONCLUSION

Different sulphated heterogeneous catalyst (Si-Ti/$SO_4^{2-}$, Si-Al/$SO_4^{2-}$, Si-Zr/$SO_4^{2-}$) has been prepared by co precipitation method and were characterized by different techniques *viz.,* SEM, XRD, FT-IR studies. Among all the prepared catalysts, Si-Zr/$SO_4^{2-}$ was found to be an effective catalyst for the esterification of oleic acid with methanol. Under the optimized reaction conditions (methanol/oleic acid molar ratio of 12:1; catalyst concentration 7 wt% at 65˚C) 97% FAME yield was obtained in 2.5 h. The esterification reaction was found to follow first order rate law with rate constant 0.02267 $min^{-1}$. Further the catalyst could be employed for 3 catalytic runs with partial decrease in catalytic activity due to the leaching of the sulphate ions from the matrix.

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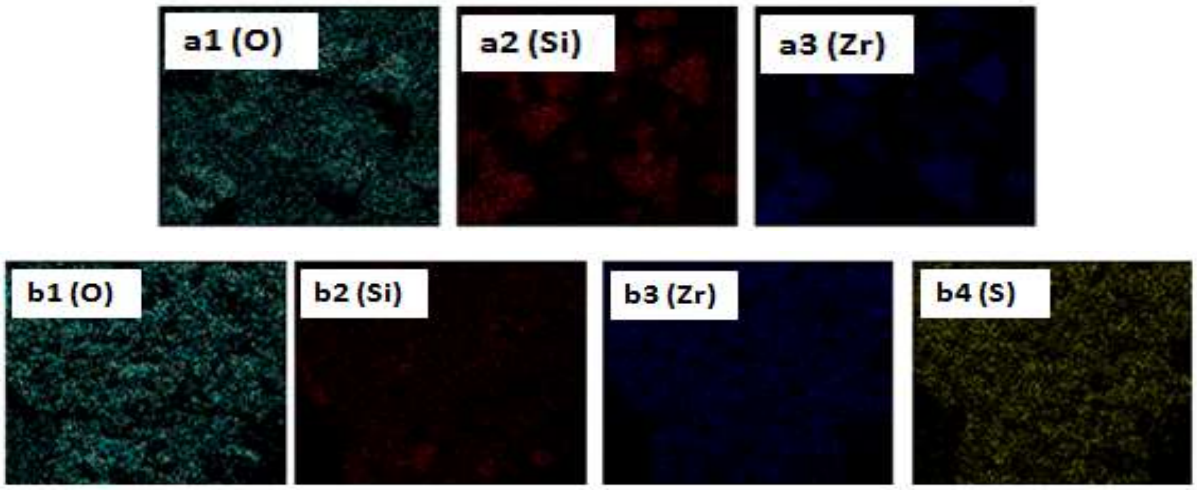
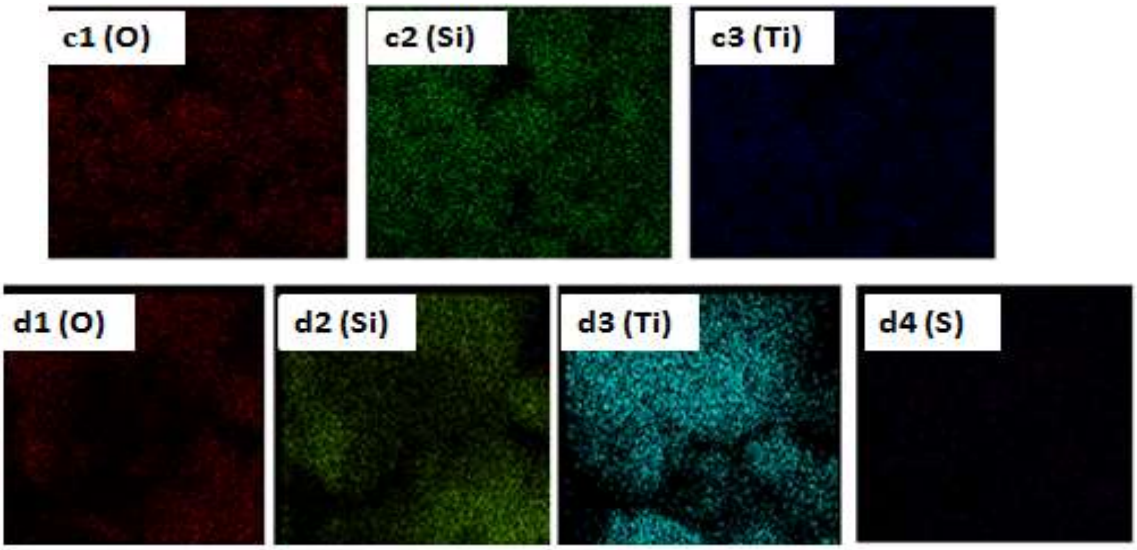
**Appendix-1**

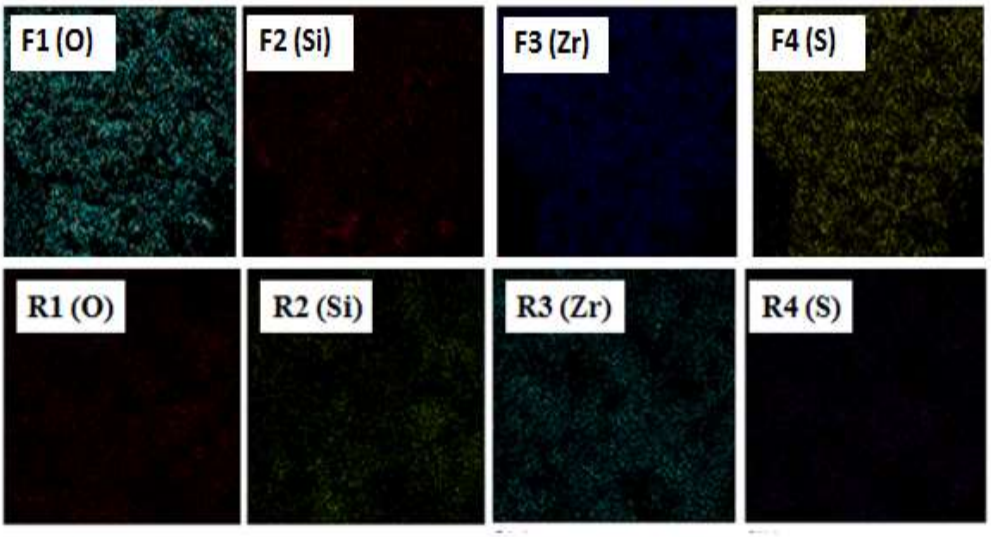



Colour elemental mapping of (a1-3) $Si(OH)_4$- $Zr(OH)_4$, (b1-4) Si-Zr/$SO_4^{2-}$.




Colour elemental mapping of (c 1-3) $Si(OH)_4$- $Ti(OH)_4$and (d 1-4) Si-Ti/$SO_4^{2-}$.

## Appendix-2




Colour **e**lemental mapping of (F1-4) Fresh and (R 1-4) Reused Si-Zr/$SO_4^{2-}$

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