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# Synthesis, Characterization and Catalytic Behaviour of Silica Supported Zinc Salicylaldimine Complex

R. K. Sharma[a]; Deepti Rawat[a]; Parul Pant[a]
[a] Green Chemistry Network Center, Department of Chemistry, University of Delhi, Delhi, India

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# Synthesis, Characterization and Catalytic Behaviour of Silica Supported Zinc Salicylaldimine Complex

R. K. SHARMA, DEEPTI RAWAT, and PARUL PANT

*Green Chemistry Network Center, Department of Chemistry, University of Delhi, Delhi, India*

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Zinc salicylaldimine complex immobilized on silica gel was used as a promising catalyst for the transesterification reaction of dimethyl terephthalate (DMT) and ethylene glycol (EG).The catalyst was characterized by Fourier transform infra-red spectroscopy (FT-IR), thermogravimetric analysis (TGA) and atomic absorption spectroscopy (AAS). The product bis-(2-hydroxyethyl)terephthalate (BHET)was confirmed by mass and $^1$H-NMR studies. In comparison to zinc acetate i.e., homogeneous catalyst, a polymer supported catalyst showed better stability, catalytic activity and ease of separation from the reaction product. The catalyst can be reutilized during successive catalytic cycles.

**Keywords:** dimethyl terephthalate; ethylene glycol; bis-(2-hydroxyethyl)terephthalate

## 1 Introduction

Transesterification is an important organic transformation to synthesize a variety of organic esters (1, 2) used in industries, as well as in academic laboratory scale reactions. Transesterification is considered more advantageous than the ester synthesis from carboxylic acids and alcohols. For instance, some carboxylic acids are sparingly soluble in organic solvents and accordingly, difficult to subject to homogeneous esterification whereas esters are commonly soluble in most of organic solvents. Transesterification of dimethyl terephthalate (DMT) with ethylene glycol (EG) in the presence of metal acetate catalyst (e.g., acetates of zinc, manganese, cobalt nickel, magnesium) (3–5) first results in the formation of BHET which acts as the monomer unit for the polymerization reaction to yield poly(ethy1ene terephthalate) (PET) (6), a versatile engineering plastic used to manufacture textiles and bottles for packaging (7–9). The decreasing catalytic activity of various metal ions for the melt transesterification of DMT and EG has been found to be in the order Zn > Ti > Sn > Sb (10). So zinc acetate was used as a homogeneous catalyst for the present study.

The separation of the homogeneous catalysts from the reaction mixture at the end of the process is the main drawback of homogeneous catalyst. A solution to this problem is to immobilize homogeneous catalyst onto inorganic support material (11–15) which allows facile recovery from the reaction mixture; hence, the selectivity and activity of homogeneous catalyst with the re-usability of a heterogeneous catalyst can be achieved simultaneously (16). In addition to this separation advantage, the catalytic performance of the immobilized catalysts (stability and selectivity), are improved as compared to their homogeneous analogs (17, 18).

In the present work, we report the immobilization of zinc salicylaldimine complex onto silica gel (Scheme 1). The catalytic activity was evaluated for the transesterification of DMT and EG at 180°C in the presence of a homogeneous catalyst (zinc acetate), physisorbed silica gel and silica gel supported zinc salicyaldimine catalysts. The main advantage of using a polymer supported catalyst is that it is easily recoverable from the reaction mixture by ordinary filtration; and hence, can be considered as a potential catalyst for industrial production of PET.

## 2 Experimental

### 2.1 Reagents

Dimethylterephthalate (Aldrich), ethylene glycol (S.D. fine chem.), 3-aminopropyltriethoxysilane (Fluka), salicylaldehyde (Sisco Chem.), zinc acetate (Thomas Baker), silica gel (Qualigens) were commercially obtained and used as such in this study.

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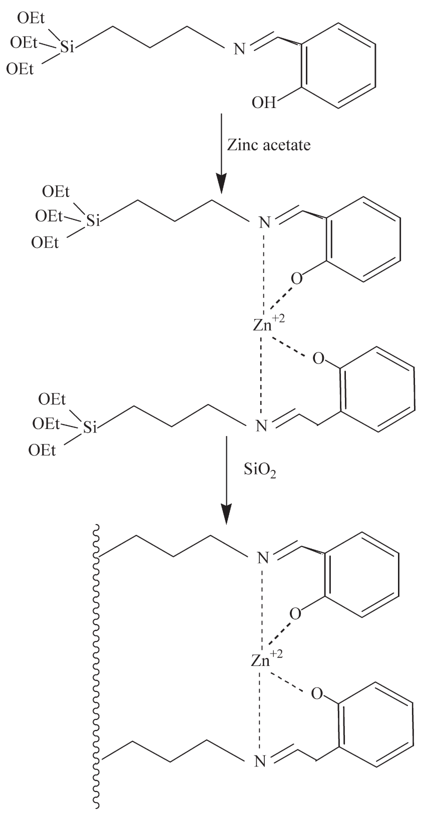
Address correspondence to: R. K. Sharma, Green Chemistry Network Center, Department of Chemistry, University of Delhi, Delhi 110007, India. Tel.: (91-11) 27666250; Fax: (91-11) 27666250; E-mail: rksharmagreenchem@hotmail.com or rksharma@chemistry.du.ac.in



**Sch. 1.** Synthetic route of the supported salicylaldimine complex.

## 2.2 Instruments

The metal content was estimated by a flame atomic absorption spectrophotometer (AA-640-13 Shimadzu) in a solution prepared by decomposing the respective catalyst in nitric acid. FTIR spectra were recorded in a KBr disk with a Perkin-Elmer spectrometer. The thermal stability of the catalysts was determined using a thermogravimetric analyzer (Perkin-Elmer TGA 7). The reaction product was confirmed by TOF-MS mass spectrometry using a Waters (USA) K-455 model with $ES^+$ mode in chloroform (HPLC grade) to investigate the molecular ion species in solution and $^1H$-NMR spectra were obtained in a Bruker 300 MHz machine, using deuterated chloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as a reference.

## 2.3 Preparation of Catalysts

To carry out the transesterification reaction, two different types of catalysts were prepared: physisorbed SG-ZnAc (catalyst 1) and silica supported salicyaldimato zinc complex (catalyst 2).

Preparation of catalyst 1: Silica gel (kept under vaccum) at 110°C was stirred overnight with ZnAc using ethanol as solvent.

Catalyst 2: Two different approaches were followed for the preparation of chemically immobilized silica supported catalyst (catalyst 2a and catalyst 2b).

Catalyst 2a was synthesized in two steps:

### 2.3.1 Synthesis of the Salicylaldiminato Complex

To 3-aminopropyl triethoxysilane APTES (2.21 g, 10 mmol) dissolved in 10 mL of dry ethanol, was added salicylaldehyde (1.22 g, 10 mmol). The resulting mixture was refluxed for 2 h. Zinc Acetate (5 mmol) was then added to a salicyaldiminato complex in dry ethanol and refluxed for 2 h.

### 2.3.2 Immobilization of the Metal Complex onto Silica Gel

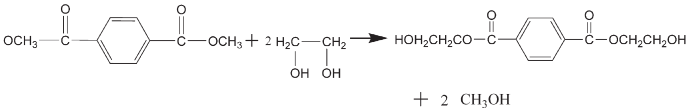
Silica gel was degassed under vacuum at 100°C. 1 g of silica gel was transferred into a 100 mL round bottomed flask and to it 100 mg (0.14 mmol) of the salicylaldimine complex was added and refluxed for 4 h. At the end of the refluxing period, the solid was filtered and washed repeatedly with toluene.

Catayst 2b: To 1 g of silica gel, 10 mmol of 3-aminopropyltriethoxysilane was suspended in dry toluene and refluxed for 24 h. The solid was separated by filtration and washed thoroughly with toluene to yield aminopropyl silica (APSG). The APSG was suspended in dry ethanol and salicylaldehyde added at a ratio of 1 mmol $(\text{g silica})^{-1}$ and refluxed for 2 h. Finally, zinc acetate was added at a ratio of 0.5 mmol of metal and the mixture was stirred for 3 h. Excess solvent was evaporated using a rotary evaporator and dried under vacuum.

## 2.4 Catalytic Reaction

The reaction involved:

1 mol DMT + 2mol EG $\rightarrow$ 1mol BHET + 2mol MeOH



The catalytic activity was studied for the transesterification of DMT and EG. The reaction was carried out in batch reactor fitted with a reflux condenser. DMT (1 mol) and polymer supported catalyst ($2.4 \times 10^{-3}$ mol corresponding to zinc acetate) was introduced into the reaction vessel and electrically heated to melting point (~140°C) of DMT. The transesterification reaction was immediately started by adding the appropriate amount of preheated EG, keeping the ratio EG/DMT = 2. The above reaction was carried out at 180°C at atmospheric pressure. The completion of the reaction was monitored by TLC. The product was isolated by column chromatography using chloroform/petroleum ether as eluent and confirmed by mass and $^1H$-NMR studies.

As this transesterification reaction is reversible, complete conversion can be achieved by elimination of formed methanol. The degree of reaction was calculated by the measurement of the quantity of methanol which is distilled from the reaction vessel. A controlled stream of nitrogen flowed through the reaction vessel to help the removal of methanol, which was collected and measured in a cold graduate trap. A similar reaction was carried out under the

**Table 1.** AAS data of different catalyst

| Catalyst | Loadings (mmolg$^{-1}$) |
|---|---|
| Catalyst 1 | 0.2 |
| Catalyst 2a | 1.2 |
| Catalyst 2b | 0.5 |

same conditions using zinc acetate as homogeneous catalyst and SG-ZnAc physisorbed catalysts.

## 3 Results and Discussion

### 3.1 *Characterization*

#### 3.1.1 *Atomic Absorption Spectroscopy*

It is seen that catalyst 2a showed higher loadings of zinc in comparison to catalyst 2b (Table 1). This result can be correlated due to the fact that in catalyst 2a metal-ligand binding is reduced in strength due to less favorable spatial orientations of ligands on the surface leading to a less robust catalyst. From the above results, catalyst 2a was taken into consideration for a transesterification reaction between DMT and EG because of higher loadings of zinc in comparison to catalyst 2b.

#### 3.1.2 *FTIR Spectra Analysis*

FT-IR spectrum of silica gel is shown in Fig. 1. Bands at 1086 and 803 cm$^{-1}$ are assigned to asymmetric and symmetric Si-O-Si stretching, respectively. Bands at 967 cm$^{-1}$ correspond to the silanol -OH group. The O-H stretching band of silanol group was observed at 3467 cm$^{-1}$.

FTIR spectrum of pure zinc acetate is shown in Fig. 2. Bands at 1550 and 1452 cm$^{-1}$ correspond to asymmetric and symmetric stretching of the carboxylate group. Bands at 694, 613 cm$^{-1}$ have been assigned to carboxylate bending and out-of-plane vibration. The band at 954 cm$^{-1}$ corresponds to C-C vibration.

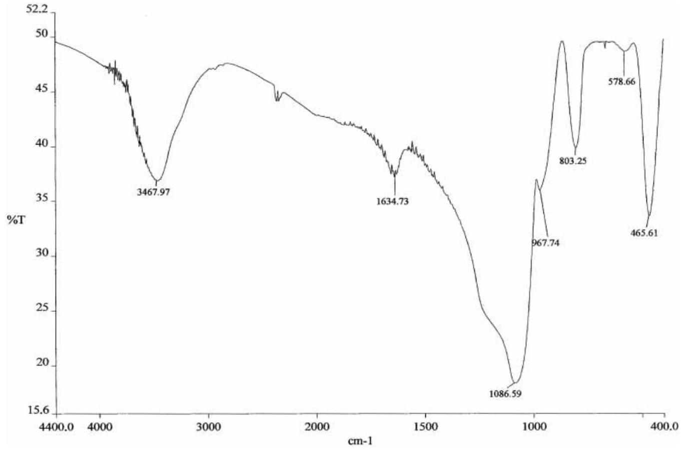


**Fig. 1.** FTIR spectra of silica gel.

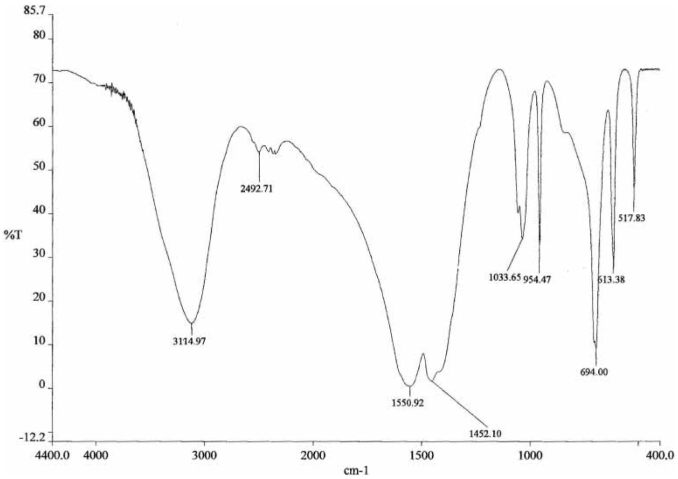


**Fig. 2.** FTIR spectra of zinc acetate.

FTIR spectrum of physisorbed SG-ZnAc is shown in Fig. 3. The presence of a band at 3435 cm$^{-1}$ corresponds to O-H stretching of silica gel. A decrease in intensity and shift of bands of carboxyl groups gave an indication of weak interaction between the hydroxyl group of SG and that of ZnAc.

FTIR spectrum of 3-aminopropyltriethoxysilane (APTES)–salicylaldehyde is shown in Fig. 4. On comparing the spectra of salicylaldehyde and APTES, it was confirmed that the immobilized salicylaldehyde onto APTS showed a band at 1664 cm$^{-1}$ which can be assigned to C=N imine formation.

FTIR spectra of the prepared catalyst is shown in Fig. 5. The band at 3049 cm$^{-1}$ corresponds to C-H stretching. Bands at 1466, 1536 cm$^{-1}$ are assigned to C=C stretching of aromatic group of salicylaldehyde. Prior to complexation with the metal, i.e., zinc showed a band at 1664 cm$^{-1}$ attributed to C=N, but on complexation with the metal, a slight shift in the band frequency of C=N was observed. This lowering in frequency of C=N was indicative of metal-ligands (ZnAc-salicylaldehyde) bond formation.

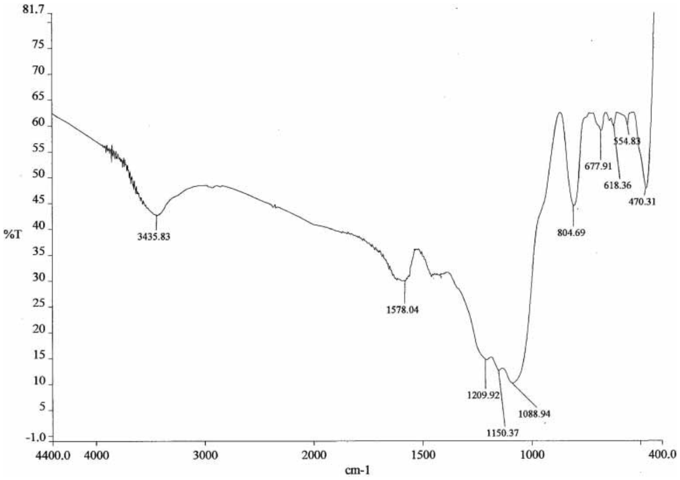


**Fig. 3.** FTIR spectra of physisorbed SG-ZnAc.

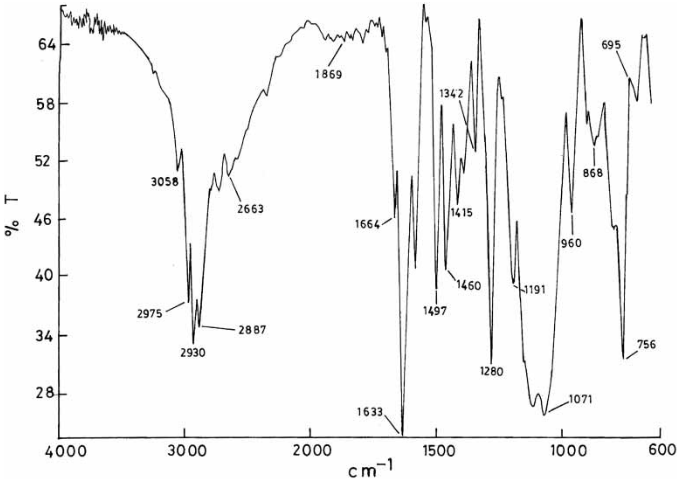


**Fig. 4.** FTIR spectra of APTES-salicylaldehyde.

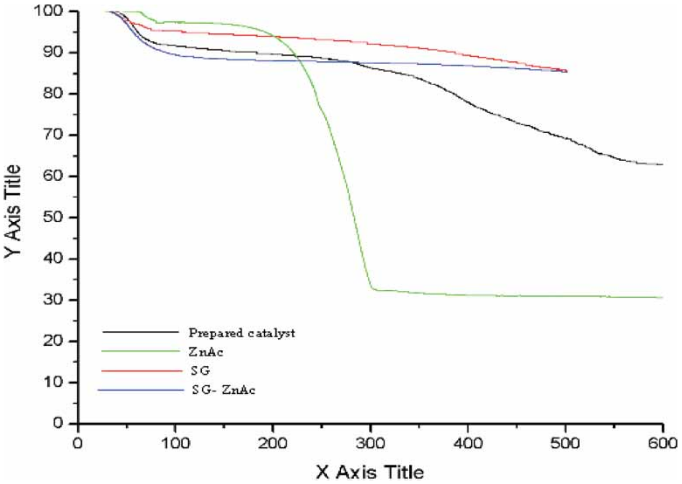


**Fig. 6.** TG curve of a) silica gel (—), b) zinc acetate (—), c) silica gel –Zinc acetate (—), d) silica supported salicyaldimato zinc complex (—).

### 3.2 *Thermal Analysis*

Thermal analysis was performed determine whether the complex on modified silica gel is stable at a temperature of transesterification reaction or not.

Thermal analysis of silica gel is shown in Fig. 6(a). Silica showed immediate weight loss with a rise in temperature. From the TG curve, there was a weight loss of 7% up to temperature 110°C. Above 100°C, the TG curve showed a broad weight loss due to dehydroxylation of silica. Total weight loss is approximately 14%.

Thermal Analysis of zinc acetate is shown in Fig. 6(b). Zinc acetate showed first weight loss in the region of 60–80°C in the TG curve. This weight loss is due to physisorbed water molecules. The second major weight loss can be seen in the region of 180–350°C and can be correlated to decomposition of the zinc complex. Thermal analysis of physisorbed SG-ZnAc is shown in Fig. 6(c). In the thermal analysis of SG-ZnAc, decomposition temperature is shifted at a higher temperature than zinc acetate, indicating that the physisorbed catalyst is stable and no decomposition occurs. Thermal analysis of prepared a polymer supported catalyst is shown in Fig. 6(d). The first weight loss corresponds to a loss of physisorbed water molecules. The second significant weight loss in the TG curve corresponds to the loss of zinc acetate in the temperature region 260–580°C, which is higher than the SG-ZnAc complex and that of pure zinc acetate. The shift of the onset temperature of decomposition of the anchored complex (i.e., catalyst) in comparison with the homogeneous catalyst (ZnAc) is attributed to covalent bonding of the complex onto the silica gel support. The TG curve reveals that the organic moieties have been combined with the inorganic support. This is consistent with the IR analysis. Because of the thermal stability of the catalyst, the transesterification reaction of DMT and EG to form BHET can be safely carried out at 180°C.

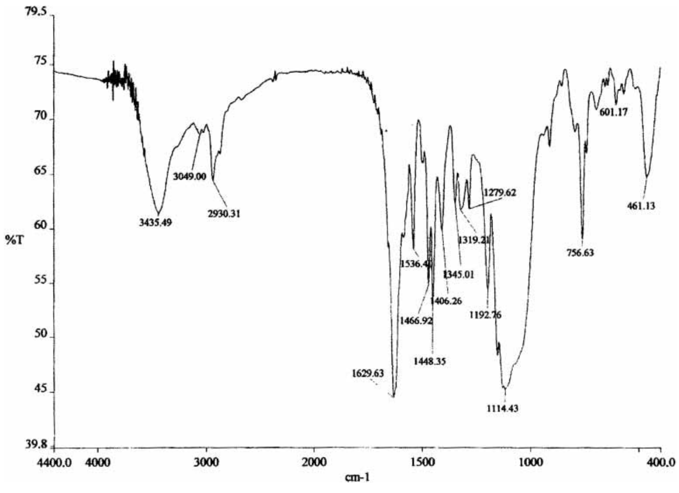


**Fig. 5.** FT-IR spectra of prepared catalyst.

### 3.3 *Mass Spectra*

The presence of strong molecular ion peak at m/z at 254 corresponds to the molecular mass of bis(2-hydroxyethyl)terephthalate (shown in Fig. 7). Mass spectra suggests that the product formed might be BHET which is further confirmed by $^1$HNMR.

### 3.4 *$^1$H-NMR*

The presence of a single peak at 8.073 ppm (shown in Fig. 8) is due to protons of the benzene ring. This signal is located at very low field because of the delocalization of electron of benzene ring. A single signal at 4.675 ppm refers to the O-H bond of formed BHET. Two triplets are also observed in the $^1$H-NMR spectra, which are attributed to the coupling of methylene groups. The presence of the first triplet at 4.468, 4.452, 4.445 ppm confers to the methylene group attached to the

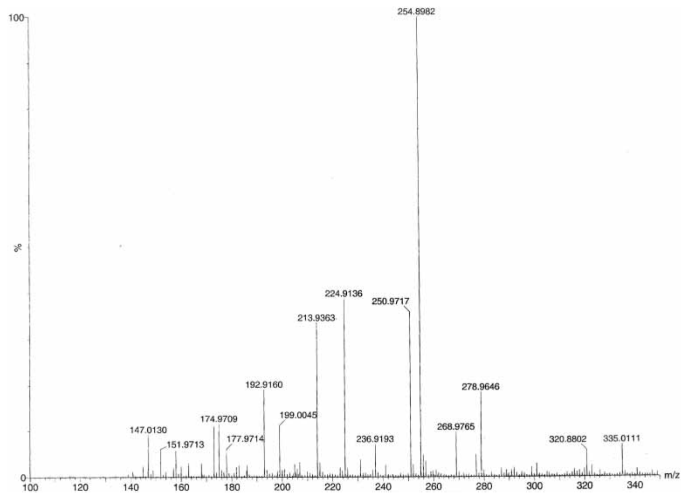


**Fig. 7.** Mass spectra of BHET.

carbonyl and second triplet at 3.960, 3.948, 3.936 ppm refers to the bonding to the hydroxyl group of BHET. NMR data reveals that the product formed corresponds to BHET. This NMR data also coincides with that of pure BHET compared to the literature. NMR analysis of the reaction product did not detect the presence of other compounds. This finding indicates that during the reaction no breaking of the bond between the silica gel supported ZnAc catalyst took place.

### 3.5 *Reaction Mechanism*

A possible transesterification mechanism in this catalyst system can be proposed as shown in Scheme 2. It has already been reported that $Zn^{2+}$ is the active catalytic species in the transesterification of DMT and EG (19, 20). The divalent metal ions, $Zn^{2+}$ acted as Lewis acids in the catalysis of transesterification. The reaction intermediate is formed by the coordination of $Zn^{2+}$ to an ester carbonyl group of DMT. The electron density of carbonyl carbon atom is then lowered by the complexation, and thus, the nucleophilic attack of the hydroxyl group of EG occurs upon this positively polarized carbonyl carbon atom resulting in a four-center transition state. The four-center transition state further lost a methanol molecule to form another intermediate. In the final step, dissociation of $Zn^{2+}$ ion from the carbonyl group completed the catalytic cycle. Similar attack takes place on the other side hence, producing ester, BHET.

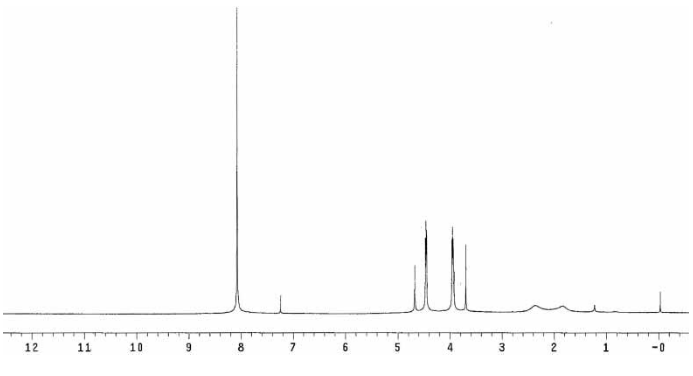
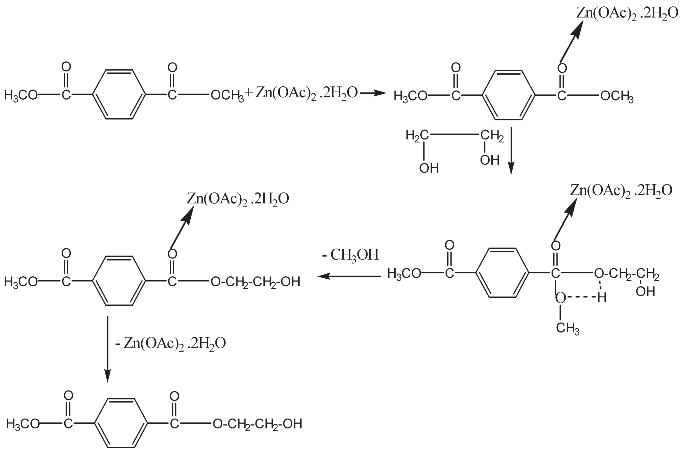


**Fig. 8.** $^1$H-NMR of BHET.



**Sch. 2.** Mechanism of transesterification.

### 3.6 *Catalytic Activity*

Catalytic activity was carried out for a number of catalysts such as:

a) Silica supported salicylaldimine complex
b) Zinc acetate (ZnAc)
c) Silica gel (SG)
d) Physisorbed Silica gel-zinc acetate (SG-ZnAc)

It has been observed that silica gel was found to be catalytically inactive and it only acts as a support to which zinc acetate is attached. Activity of the transesterification revolves around the metal center. Activity of physisorbed SG-ZnAc, where zinc acetate was refluxed with unfuctionalized silica gel was found to be lower than that of the homogeneous catalyst (i.e., ZnAc). This is due to the fact that some of the zinc acetate gets blocked inside the porous structure of silica gel and is not readily accessible to the reactants.

Activity of the prepared catalyst was found to be higher that of the homogeneous catalyst. In the prepared catalyst, zinc acetate is chemisorbed and supported on functionalized silica gel through salicylaldehyde, so less zinc ions is lost during the reaction and a number of catalytically accessible active sites is much higher as compared to that of SG-ZnAc.

### 3.7 *Reuse, Regeneration, and Recycling of the Catalyst*

After completion of the transesterification reaction, silica supported zinc acetate catalyst could be easily recovered from the reaction mixture by filtration and was reused several times without any discernable change of activity.

The regeneration of the catalyst was achieved by treating the reused catalyst with zinc acetate in chloroform at room temperature. It was washed with acetone, and dried under vacuum at 50°C for 24 h. The catalyst showed the original catalytic activity. The recycling process can be repeated several times without appreciable loss of activity, and the resulting catalyst can be used for subsequent reactions.

## 4 Conclusion

A salicylaldiminato complex of zinc was immobilized onto amorphous silica and examined for the transesterification of DMT and EG. Thermal analysis of the catalyst revealed that the prepared catalyst was found to be stable at a reaction temperature of 180°C. $^1$H-NMR of the product confirmed the formation of BHET and revealed that it did not contain any traces of supported catalyst. We expect that this new approach to the immobilization of complexes would permit the tailored synthesis of highly active,stable and reusable catalysts for fine chemicals production.

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